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OF THE
NATIONAL BUREAU OF STANDARDS

Vol. 14 MARCH 1935 No. 3

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JOURNAL OF RESEARCH
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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP766

Part of Journal of Research of the National Bureau of Standards, Volume 14, March 1935

MONITORING THE STANDARD RADIO-FREQUENCY EMISSIONS

By Evan G. Lapham

ABSTRACT

The method and equipment used in monitoring the standard frequency emissions are described in this paper. The emissions are continuously recorded in terms of the primary standard of frequency maintained by the Bureau. By means of selector circuits and frequency multipliers the received signal is heterodyned with the appropriate harmonic of the primary standard. The beat frequency is then recorded on a recording potentiometer by means of a circuit arrangement which produces a potential difference that is proportional to the frequency difference. The records show that the emissions have been in agreement with the primary frequency standard within two parts in one hundred million at practically all times, and the absolute value of the frequency transmitted is rarely in error by as much as one part in ten million.

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I. INTRODUCTION

The radio transmitting station of the National Bureau of Standards is located near Beltsville, Md.,[1] which is about 13 miles northeast of the Bureau's principal radio laboratory. Standard radio frequencies are transmitted regularly from the Beltsville station. Prior to February 1, 1935 [2] an unmodulated wave having a frequency of 5,000.000 kc/s was transmitted each Tuesday from noon to 2 p. m., and from 10 p. m. to midnight, EST. The transmitted frequency is obtained by means of suitable frequency multipliers from a piezo oscillator,[3] located at the transmitting station, which has a fundamental frequency of 200 kc/s. A precise frequency adjustment is provided on this standard so that the transmitted frequency can be readily brought into exact agreement with the primary frequency

[1] BS J. Research **12**, 1 (1934) RP630.

[2] Beginning February 1, 1935, and continuing each Tuesday and Friday thereafter (except legal holidays), three frequencies will be transmitted as follows:

Time (EST)	kc/s
12 noon to 1 p.m.	15,000
1:15 to 2:15 p.m.	10,000
2:30 to 3:30 p.m.	5,000

[3] BS J. Research **11**, 59 (1933) RP576.

standard [4] in the principal radio laboratory, Washington, D. C. Although the standard at the transmitting station normally maintains agreement with the primary frequency standard within the desired limits for a period of 2 hours, which is the duration of a standard frequency emission, frequency comparisons against the primary standard are made continuously during the emissions, so that a readjustment of the frequency could be made if it became necessary and also as a check on the proper operation of the transmitter. Special apparatus was developed which automatically records the frequency difference between the transmitted frequency and the primary standard.

II. METHOD USED IN MAKING FREQUENCY MEASUREMENTS

The method used in making the frequency measurements is indicated schematically in figure 1. Receiver no. 1 is connected to the antenna and to one of the outputs of the auxiliary oscillator. The frequency of the auxiliary oscillator is approximately 1000.120 kc/s. The receiver being tuned to 10,000 kc/s amplifies the second harmonic of the signal received from the transmitter and the tenth harmonic of the frequency of the auxiliary oscillator. The two signals, which are amplified by receiver no. 1, differ by 1,200 cycles per second. The result is that an audiofrequency of 1,200 cycles per second is produced in the output of this receiver. The other receiver, no. 2, is connected to the output of one of the units of the primary standard, no. 6 in figure 1, and output of the auxiliary oscillator. This receiver is likewise tuned to 10,000 kc/s and thus amplifies the one-hundredth harmonic of the primary standard and the tenth harmonic of the auxiliary oscillator. Assuming the frequency of this primary standard to be 100.00004 kc/s, the two frequencies amplified by this receiver differ by 1,196 cycles per second and an audiofrequency of 1,196 is produced in the output of receiver no. 2. The outputs of the two radio receivers are then combined and connected to an audiofrequency amplifier. These two audiofrequencies alternately reinforce and interfere so that the resulting output of the audiofrequency amplifier carries a frequency which is equal to the difference between the two audiofrequencies, or 4 cycles per second in the example cited. If one calculates the frequency difference between the second harmonic of the transmitted signal and the one-hundredth harmonic of the primary standard, it is seen that it is 4 cycles per second. The beat frequency on the output of the audiofrequency amplifier, thus, is the difference between the frequency of the primary standard, no. 6, and the second harmonic of the transmitted signal, and is independent of the frequency of the auxiliary oscillator, the latter serving only to provide a carrier frequency. In order to determine the frequency of the transmitter at any given instant it is necessary to measure this beat frequency. For this purpose a special form of beat recorder was developed. The frequency of the transmitter can then be calculated if it is known whether the transmitter is higher or lower than the corresponding harmonic of the primary standard. The direction of the difference is determined by making a check against another unit of the primary standard which is known to be higher or lower than the one previously used.

[4] Elmer L. Hall, Vincent E. Heaton, and Evan G. Lapham. *The national primary standard of radio frequency.* BS J. Research **14,** 85 (1935) RP759.

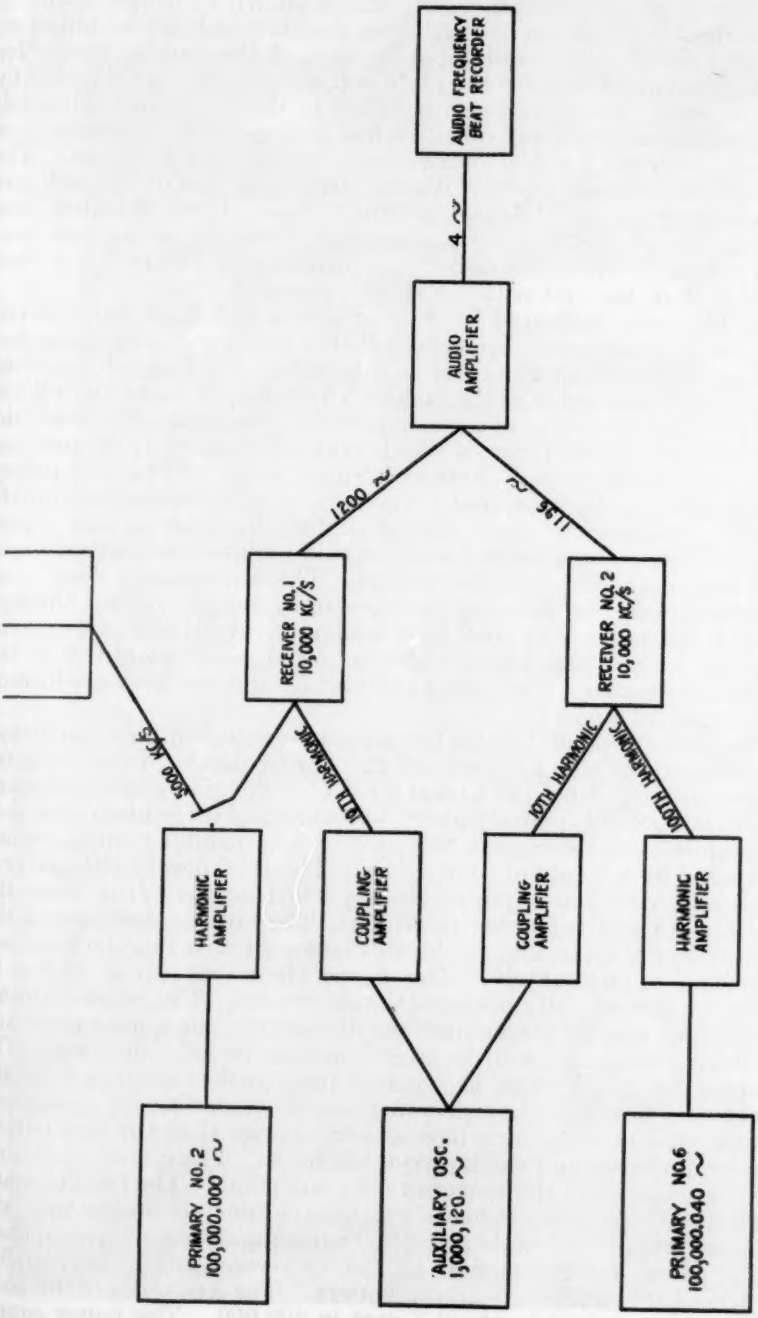

FIGURE 1.—*Schematic diagram of standard frequency monitor.*

III. DESCRIPTION OF EQUIPMENT

The complete monitoring equipment is shown in figures 2 and 3. The various sections are assembled on panels which are mounted on two relay racks. The equipment on each of the panels, except for the rectifiers and filters for the plate voltage supplies, are shielded by metal covers. The shields are fastened to the horizontal subpanels by thumbscrews, and phosphor-bronze springs make low-resistance contacts with the vertical panel along the top of the covers. The connections between circuits which carry radio-frequency voltages are made by means of concentric tube lines. These shielded lines are constructed of ⅝-inch brass tube with ⅛-inch brass rod held centrally within it by means of bakelite insulators. Figure 3 is a view of the back of the unit with the shields removed.

The receivers, indicated by A in figures 2 and 3, are commercial receivers of the regenerative type. Either receiver can be connected to an outside antenna by means of the double-throw switch mounted in the center at the top of the racks. They may be tuned from 2,500 to 25,000 kc/s by means of interchangeable coils, making possible the measurements of frequencies which are multiples of 1,000 between 3,000 and 25,000 kc/s. There is a single stage of radio-frequency amplification, a detector, and two stages of audiofrequency amplification. The receivers were altered slightly in order to incorporate an automatic volume control which would maintain a relatively constant audiofrequency output voltage. The automatic volume control was obtained by shunting a portion of the output voltage through a copper-oxide rectifier and filter and applying this direct-current potential to the grid bias on the radio-frequency amplifier in the customary manner. The power supplies for the receivers are located at B in figures 2 and 3.

The auxiliary oscillator is a temperature-controlled piezo oscillator. It is indicated by C in figures 2 and 3. The frequency of this oscillator is approximately 1000.120 kc/s at 50.8° C. The piezoelectric element is a circular, X-cut quartz plate. The quartz-plate holder consists of two stainless-steel electrodes mounted in a horizontal position, which are spaced by a toroid of pyrex glass. The thickness of the spacer is such that an air gap of approximately 0.004 inch is left between the quartz plate and the upper electrode. The outside diameter of the pyrex spacer is 1¾ inches, the inside diameter 1 inch, and the thickness 0.15 inch, approximately. The pyrex glass spacer also serves to retain the quartz plate between the electrodes. The inner diameter is only very slightly larger than the diameter of the quartz plate and therefore permits very little lateral motion in any direction. The damping produced when the quartz plate makes contact with the spacer was minimized by grinding the inner surface of the spacer slightly conical from each face in such a way that the two conical surfaces intersect midway between the faces. The quartz plate thus makes contact with the spacer at only one point. The oscillator and amplifier circuit arrangements are conventional in every way and therefore require no explanation. Two separate coupling amplifiers are provided for connection to the two receivers. The coupling capacitors are variable 15-$\mu\mu$f condensers. The frequency of this piezo oscillator is constant to about 1 part in 300,000. The power supply for the piezo oscillator is shown at E in figures 2 and 3. A UX874

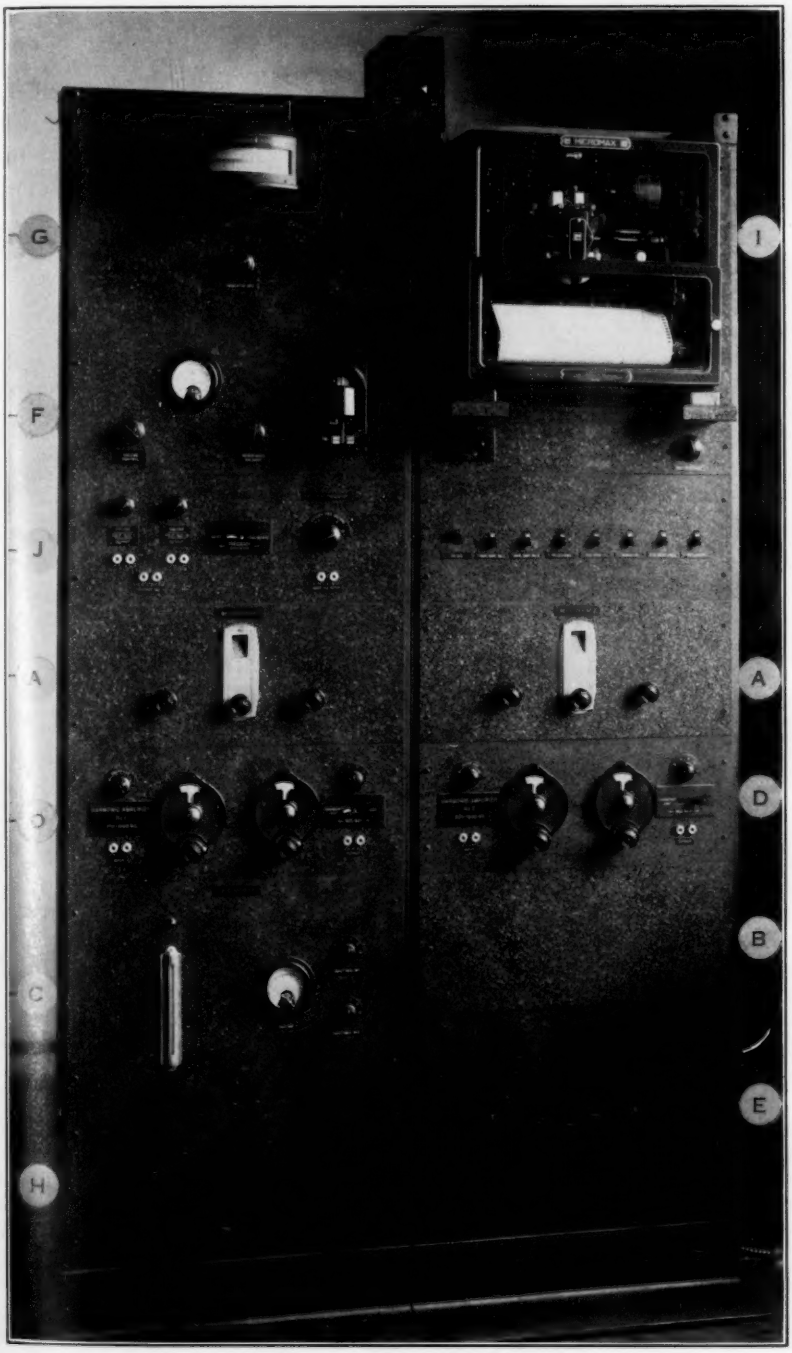

FIGURE 2.—*Front view of the standard frequency monitor.*

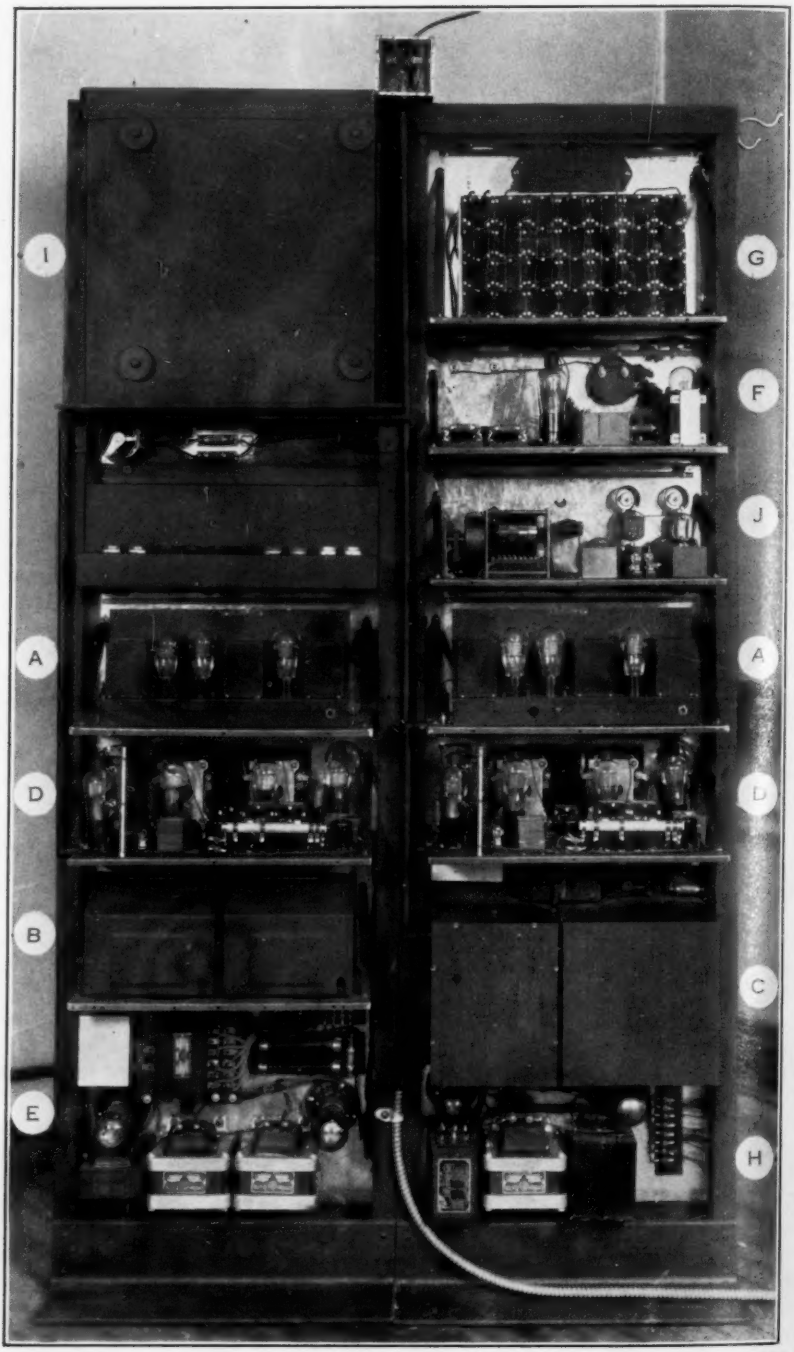

FIGURE 3.—*Rear view of the standard frequency monitor with the shields removed.*

voltage-regulator tube is used to supply the plate voltage for the oscillator tube.

The plate and filament voltages for the harmonic amplifiers are also supplied by the rectifier and filament transformer on the panel at E. The two harmonic amplifiers are shown at D. These units consist of an impedance-coupled input amplifier, two tuned amplifier stages, and an impedance-coupled output amplifier. In one of these units the first tuned amplifier is tuned to 200 kc/s and the second to 1,000 kc/s. This harmonic amplifier has an output of 1,000 kc/s with an input of 100 or 200 kc/s. The other harmonic amplifier has the tuned amplifiers adjusted to 500 and 1,000 kc/s, respectively, and gives an output of 1,000 kc/s with an input of 100 or 500 kc/s. The type 224 tube is used in these amplifiers.

Considerable difficulty was encountered in preventing the input voltage to one of the harmonic amplifiers from feeding into the other. The interaction between these two units was eliminated by having separate voltage dividers and 60-mh radio-frequency chokes in both the positive and negative leads of the plate voltage supply. The output of the harmonic amplifiers can either be connected to the receiver or to the jacks on the front panel, if used for other purposes, by means of the two-way switch on the right of each panel. When the switch is in the position to connect the output to the jacks, the receiver on the panel above can be connected to the antenna by properly setting the antenna switch previously mentioned. If the output of the harmonic amplifier is connected to the receiver the antenna connection is grounded. A 15-$\mu\mu$f variable condenser is provided to control the voltage input to the receiver.

The equipment used in measuring the beat frequency between the transmitted signal and the primary frequency is shown at F, G, H, I, and J, figures 2 and 3. The circuit arrangement is shown in figure 4. The voltage divider and voltage-regulator tube are mounted with the power pack for this unit on the panel H. The remainder of the circuits are on the panels F and G. The outputs of the two receivers are connected to the audiofrequency amplifier. The output of this amplifier is rectified by means of two half-wave copper-oxide rectifiers, Q, of the type used in rectifier type alternating-current meters, connected in a familiar voltage doubling arrangement. By rectifying the audiofrequency output a unidirectional potential is produced, which is the envelop of the two audiofrequency notes. This direct-current potential is connected as shown, to the grids of two type UY235 tubes. The plate impedance for these tubes is a 10,000-ohm voltage divider and the variable contact is used to balance the currents in the two tubes. The screen grid and plate are connected together as shown. A sensitive, polarized relay is connected across the plate resistor in series with a zero-center milliammeter which serves as a beat indicator. When the audiofrequency voltage reaches a maximum the resulting direct-current potential charges the 1-μf condenser, L, positively through the 2-megohm grid resistor, making this grid less negative, which accordingly increases the plate current in this tube. At the same time the 1-μf condenser, M, is charged negatively and the current in this tube is decreased. The result is that a difference of potential is produced across the plate resistor, a current flows through the coil of the polarized relay and the reed moves in one direction. When the audiofrequency

voltage decreases to a minimum the 1-μf condensers discharge through the 2-megohm grid resistors, which reverses the change in bias on the tubes, the potential difference across the plate impedance is in the opposite sense, and the relay reed moves in the opposite direction. The combination of coupling condenser and grid resistor which is used must be one which has a charging time somewhat greater than one-fourth the period of the modulation frequency. The comparatively slow rate of charge and discharge of the 1μf condenser through the 2-megohm resistor serves to prevent noise of short duration from interfering with the operation of the relay. The particular values used in this case make the relay operate over a range from 0.2 cycle per second to approximately 25 c/s. When the relay makes contact in one position, a 0.1-μf condenser is charged to 90 v, and when it makes contact in the other position the condenser is discharged completely into a condenser having a capacity of approximately 112 μf. The 112-μf condenser discharges slowly through a 50,000-ohm resistor connected in series with a microammeter. After the relay has operated at a given frequency for a short time the voltage in the 112-μf condenser reaches an average value which is proportional, approximately, to the frequency operating the relay. The current through the microammeter is consequently approximately proportional to the frequency, and the instrument can be calibrated to read frequency directly. The record of the frequency variations is obtained by connecting a recording potentiometer across a portion of the 50,000-ohm resistor which is in series with the microammeter. The Leeds & Northrup recording potentiometer, I, in figures 2 and 3, has been found to operate very satisfactorily for this purpose. The principal requirement is that the galvanometer have a high sensitivity and a low natural frequency. By adjusting the voltage across the slide wire the recorder is likewise made direct reading. The 90-v supply which charges the 0.1-μf condenser also supplies the voltage for the potentiometer, which makes the recorder moderately independent of voltage fluctuations. The frequency-indicating meter reads from 0 to 9 c/s with the smallest division 0.1 c/s or one part in one hundred million at 10,000 kc/s. The recorder covers the range from 0 to 5 cycles per second, with the smallest division 0.05 c/s or one-half part in one hundred million at 10,000 kc/s.

In order to be able to readily calibrate the frequency-indicating meter and recorder it was necessary to have a source of known frequency with which to operate the beat-frequency measuring equipment. This was provided by constructing a device which would interrupt a 1,000-cycle voltage at a known rate. The 1,000-cycle voltage was used in this case as it was available in the laboratory, but practically any audiofrequency, such as a small 60-cycle voltage from the power line, would be satisfactory. The interrupting device, J, in figures 2 and 3, consisted of a 5-w telechron motor which was geared to turn a shaft at the rate of 12 revolutions per minute. Four separate insulating disks were mounted on this shaft. One of the disks had two metal segments equally spaced on the cylindrical surface. The space between segments was equal to the length of the segments. Two phosphor-bronze springs pressed against this disk in such a way that they were connected together at the times that the metal segment was passing under them. The 1,000-cycle voltage was connected so that it was in series with these sliding contacts. One revolution of

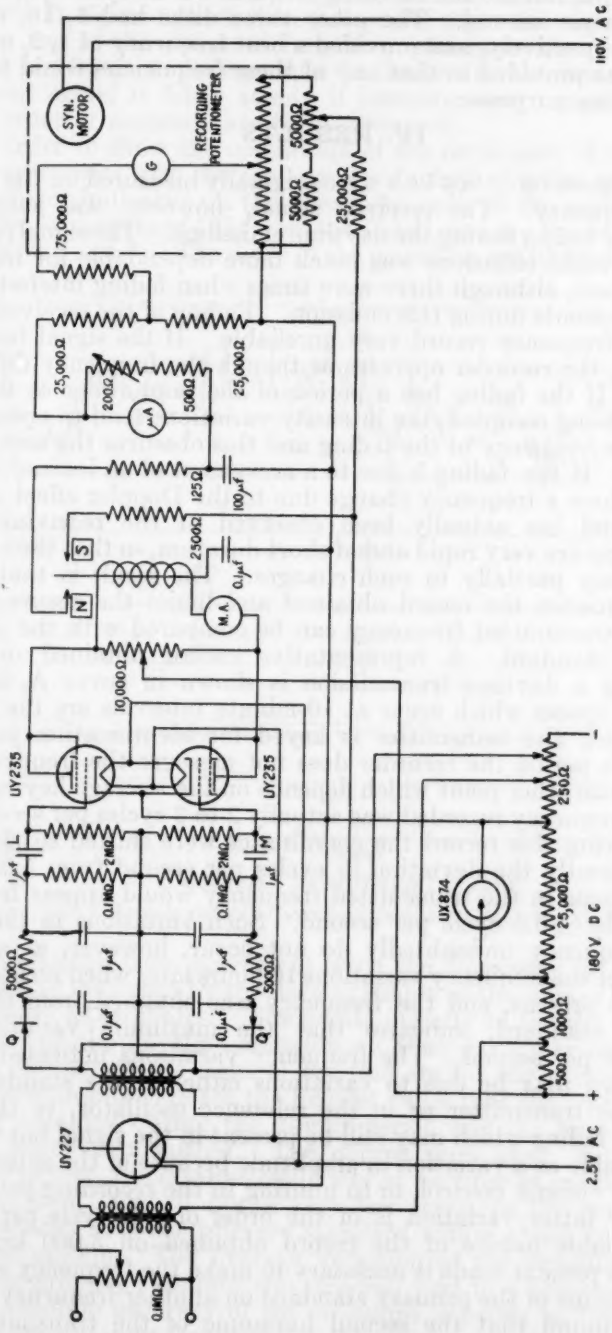

FIGURE 4.—*Circuit arrangement of the beat indicator and recorder*

this disk completed 2 cycles. With the disk rotating at the rate of 12 revolutions per minute the resulting frequency is 24 cycles per minute or 0.4 cycle per second. The other three disks had 5, 10, and 15 segments, respectively, and provided a beat frequency of 1, 2, or 3 c/s. A switch was provided so that any of these frequencies could be used for calibrating purposes.

IV. RESULTS

The emissions on 5,000 kc/s were originally measured on the fundamental frequency. The received signal, however, was subject to considerable fading during the daytime emissions. The signal received during the night emissions was much more dependable for measurement purposes, although there were times when fading intefered with the measurements during this emission. Fading of the received signal makes the frequency record very unreliable. If the signal fades out completely, the recorder operates as though the frequency difference was zero. If the fading has a period of the same order as the beat frequency being recorded, the intensity variations tend to operate the relay at the frequency of the fading and this obscures the actual beat frequency. If the fading is due to a movement of an ionized layer in the ionosphere a frequency change due to the Doppler effect is to be expected and has actually been observed at the receiving point. Such changes are very rapid and of short duration, so that the recorder responds only partially to such changes. The result is that fading tends to broaden the record obtained and limits the accuracy with which the transmitted frequency can be compared with the primary frequency standard. A representative record obtained on 5,000 kc/s during a daytime transmission is shown in curve A, figure 5. The blank spaces which occur at 10-minute intervals are the periods during which the transmitter is keyed for identification purposes. During this period the recorder does not measure the frequency but drops to some other point which depends on the average keying speed. The beat frequency recorded was actually 2 to 3 cycles per second, but in reproducing this record the coordinates were shifted so that they indicate directly the deviation in cycles per second from 5,000 kc/s. The variations in the transmitted frequency would appear from this record to be ± 0.5 cycle per second. Such variations in the transmitted frequency undoubtedly do not occur, however, as a record (curve B) of the frequency variations 10 hours later when no noticeable fading was present, and the frequency was obtained from the same frequency standard, indicates that the maximum variations are ± 0.1 cycle per second. The frequency variations indicated by the latter record may be due to variations either in the standard controlling the transmitter or in the reference oscillator, to the small amount of fading which may still be present in the signal but which is not noticeable as a variation in amplitude because of the action of the automatic volume control, or to hunting in the recording potentiometer. The latter variation is of the order of 0.02 cycle per second. The unreliable nature of the record obtained on 5,000 kc/s when fading was present made it necessary to make the frequency measurements in terms of the primary standard on another frequency.

It was found that the second harmonic of the transmitted frequency, 10,000 kc/s, was sufficiently strong at the laboratory in Washington, D. C., to be measured and recorded dependably. The

signal received on the second harmonic, moreover, was free from fading, and records indicate frequency variations of the order of those in curve B, figure 5, both during day and night emissions.

The use of the standard frequency emissions where the received signal is subject to fading must be limited to the periods when the received signal is fairly steady if instantaneous measurements of a high order of accuracy are to be obtained.

In order to show the magnitude of the deviations of the emissions from agreement with the primary standard, the highest and the lowest frequencies indicated on the record for each of the emissions during the first 10 months of 1934 were tabulated, and are presented in curves A, figures 6 and 7. The dates of the emissions are plotted as abscissas.

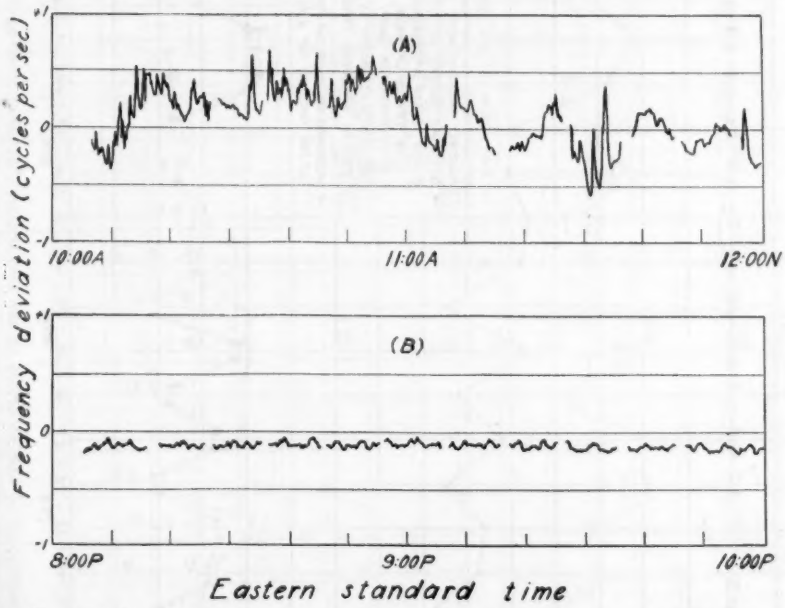

FIGURE 5.—*Sample record of standard frequency emission on 5,000* kc/s

The deviations from agreement with the frequency of the primary standard as indicated by the data available at the time of the emission are plotted as ordinates. The points directly to the left of a vertical line are for the daytime emission on that particular date, and the points directly to the right of the line are for the evening emission. The upper points indicate the highest value that the transmitted frequency attained during the 2-hour period and the lower points the lowest value transmitted. The curves show that, during the 10-months period, the disagreement was at no time as great as one part in 10 million. On all but a very few occasions the emissions were in agreement with the primary standard within about two parts in a hundred million. The average variation of the emission frequency from the primary standard was one-half part in a hundred million.

The absolute accuracy of the emissions depends on the determination of the absolute frequency of the primary standard. The determination of the frequency of the primary standard is made by com-

paring the time indicated by a synchronous-motor clock controlled by one of the standards with standard time. The time signals received by radio from the Naval Observatory are used for this purpose. Since the time signals are somewhat in error, corrections are sent out by the Naval Observatory. These corrections were formerly received

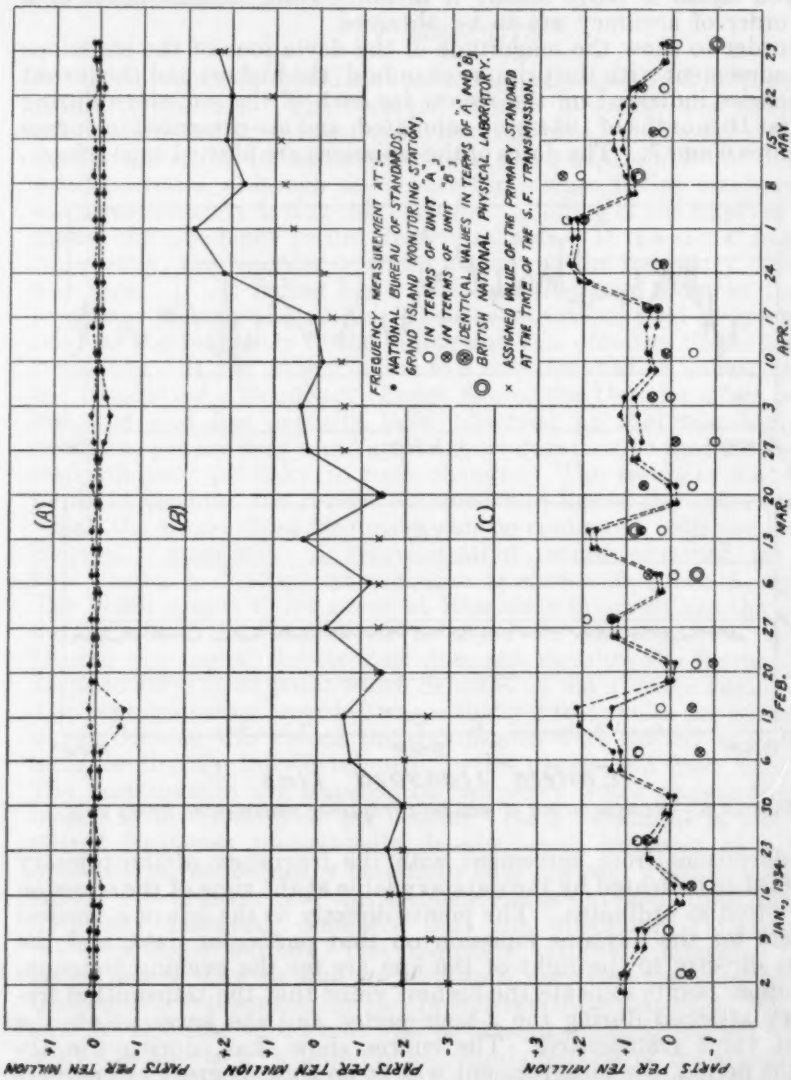
(A)
(B)
(C)
FREQUENCY MEASUREMENT AT:—
• NATIONAL BUREAU OF STANDARDS, GRAND ISLAND MONITORING STATION,
○ IN TERMS OF UNIT "A".
⊗ IN TERMS OF UNIT "B".
◎ IDENTICAL VALUES IN TERMS OF "A" AND "B".
BRITISH NATIONAL PHYSICAL LABORATORY.
× ASSIGNED VALUE OF THE PRIMARY STANDARD AT THE TIME OF THE S. F. TRANSMISSION.
PARTS PER TEN MILLION
PARTS PER TEN MILLION
PARTS PER TEN MILLION
JAN., 1934
FEB.
MAR.
APR.
MAY

FIGURE 6.—*Graphical representation of the accuracy of the emissions, January to May 1934.*

(A) deviations of emissions from assigned value of primary standard; (B) assigned and corrected values of a unit of primary standard in parts in ten million above or below 100 kc/s; (C) deviation of emissions from corrected value of primary standard.

a month or more late, although recently the delay in the receipt of the corrections has been reduced to about 1 week. The frequencies as calculated in terms of the uncorrected time signals show variations of the order of four parts in 10 million. For the standard frequency emissions it is necessary to extrapolate a curve through these points. After the corrections are received the variations in the frequency as

indicated by the time checks are narrowed down to approximately one part in 10 million. For this reason the value of the primary standard assigned at the time of the emission differs from the final corrected value. Curves B, figures 6 and 7, give the frequency, on the date of the emission, of one of the units of the primary standard which was checked against standard time during this period. The solid line

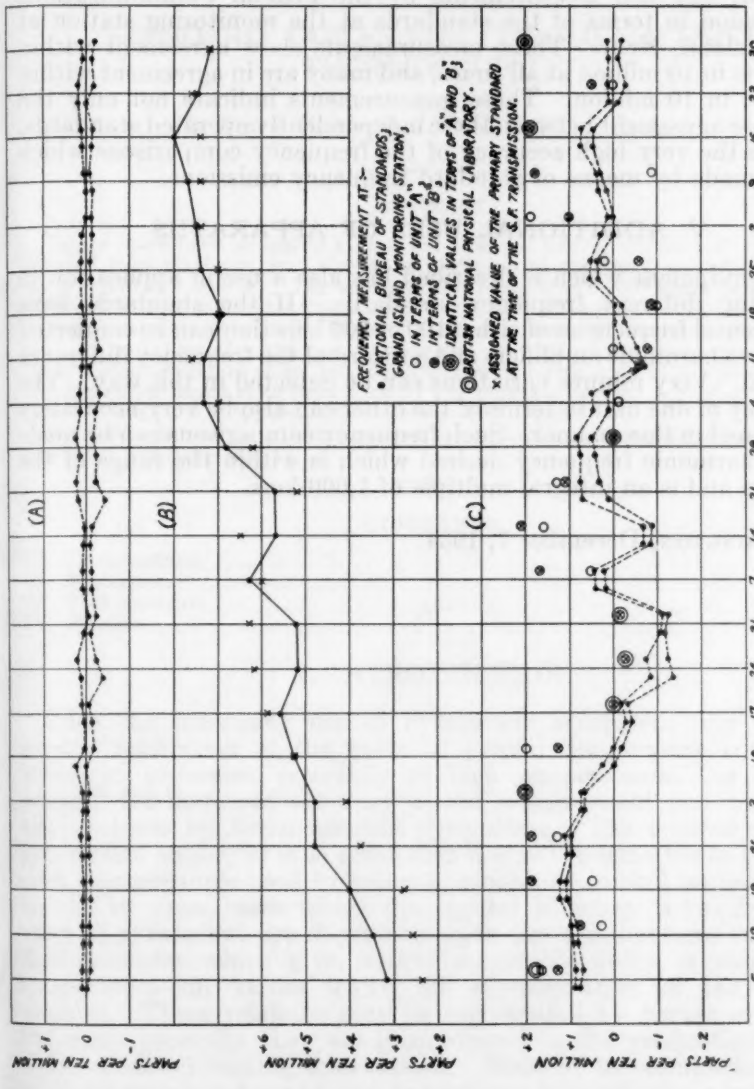

FIGURE 7.—*Graphical representation of the accuracy of the emissions, June to October 1934.*

(A) deviations of emissions from assigned value of primary standard; (B) assigned and corrected values of a unit of primary standard in parts in ten million above or below 100 kc/s; (C) deviation of emissions from corrected value of primary standard.

indicates the corrected values and the crosses the frequencies which were assigned at the time of the emissions. This error in the frequency of the primary standard decreases the absolute accuracy of the standard frequency emissions by a corresponding amount, as shown in curves C, figures 6 and 7, which give the transmitted frequency as determined in terms of the corrected values of the primary standard.

It is seen that the absolute value of the transmitted frequency was rarely in error by as much as one part in 10 million.

An interesting check on the measurements made at the National Bureau of Standards is shown in curves C, figures 6 and 7. Frequency comparisons are given which have been reported by the British National Physical Laboratory in terms of their national primary standard, and also measurements by the Federal Communications Commission in terms of the standards at the monitoring station at Grand Island, Nebr. These measurements show agreement within two parts in 10 million at all times, and many are in agreement within one part in 10 million. These measurements indicate not only the very close agreement between these independently operated standards, but also the very high accuracy of the frequency comparisons which can be made by means of standard frequency emissions.

V. ADDITIONAL USES OF APPARATUS

The equipment which is described has also a useful application in comparing different frequency standards. If the standards have fundamental frequencies of either 100 or 200 kc/s they can be connected to the two harmonic amplifiers and a record of the frequency difference obtained. Very minute variations can be detected in this way. The frequency of one unit in terms of the other can also be very accurately determined in this manner. Such frequency comparisons can be made at any harmonic frequency desired which is within the range of the receivers and is an integral multiple of 1,000 kc/s.

WASHINGTON, December 7, 1934.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP767

Part of Journal of Research of the National Bureau of Standards, Volume 14, March 1935

STANDARD TABLES FOR CHROMEL-ALUMEL THERMOCOUPLES

By Wm. F. Roeser, A. I. Dahl, and G. J. Gowens

ABSTRACT

Tables have been prepared giving the thermal emf of chromel P vs alumel, chromel P vs platinum, and alumel vs platinum at various temperatures in the range −310 to 2,500° F. The values in the range 0 to 2,500° F are based on the calibration of 15 representative no. 8 gage chromel-alumel thermocouples selected after preliminary tests on 50 heats of each alloy made by the method regularly used. The tables give the temperature-emf relation of the thermocouples now being manufactured as closely as the wires can be reproduced at the present time. The guarantee limits have been fixed by the manufacturer at ±5° F in the range 0 to 660° F and to ±¾ percent in the range 660 to 2,300° F.

The methods used in calibrating the thermocouples in the various temperature ranges are briefly described.

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I. INTRODUCTION

With the increasing use of pyrometric equipment and a more general realization of the value of careful temperature control of industrial processes, especially at high temperatures, has come a demand for increased accuracy in the measurement and control of temperatures by thermoelectric pyrometers. The number of such pyrometers employed is so great that it is not practicable to calibrate each thermocouple used to indicate, record, or control temperatures. Except in those cases where the highest accuracy is required, the users of pyrometers are dependent upon the manufacturer to supply thermocouples which give, within reasonable limits, corresponding temperature-emf values which are representative of the general product. These relations may be represented by curves or tables, but more generally they are incorporated in the graduation of the scales of direct-reading instruments. Some of the temperature-emf relations now in use are of such nature that it is difficult or impossible to make thermocouples to correspond to them. There are a number of tables published in catalogs, handbooks, and physical tables giving corresponding temperature-emf values for thermocouples, but it has not been demonstrated, except in the case of rare-metal thermo-

couples,[1] that any of these tables represent, to the accuracy demanded, the temperature-emf relation of the couples now being manufactured.

The variety of tables used for chromel-alumel has not been as great as for other types of base-metal couples, because there has never been more than one manufacturer of this type of couple. Although the differences among the various tables published in the past twenty years for chromel-alumel thermocouples are not large, they are greater than the errors permissible in many industrial and technical processes. These differences cannot be attributed entirely to variations in the characteristics of the thermocouples as produced at various times. Many of them are due to the methods of arriving at the tables; for example, as concerns the accuracy of the measurements, number of observations, number of thermocouples used, and the degree to which the material tested was representative of the general product.

At the request of a number of pyrometer users and instrument manufacturers, and in cooperation with the Hoskins Manufacturing Co., the present investigation was conducted at the National Bureau of Standards to determine a representative temperature-emf relation for the chromel-alumel thermocouples now being manufactured.

II. MATERIALS

The nominal composition of the chromel P alloy is 90-percent nickel and 10-percent chromium. Alumel contains approximately 95 percent nickel, with aluminum, silicon, and manganese making up the other 5 percent.

Approximately 80 percent of the chromel P and alumel used in thermocouples is no. 8 gage wire and 95 percent is no. 6, 8, 11, and 14 gage wire. As the shape of the temperature-emf curve is apparently independent of the size of the wire, only no. 8 gage wire was used in the present work. The manufacturer selected 30 samples of no. 8 gage wire from 100 heats of chromel P and alumel. In order that the completed thermocouples should be typical of the general product, all of this wire was heat treated and "matched" by the manufacturer in the same manner as all the chromel P and alumel wire regularly supplied to pyrometer users. The process of matching consists in measuring the thermal emf of each lot of chromel P and of alumel against pure platinum at one or more selected temperatures, and then combining the lots of chromel P and of alumel so that the completed thermocouples will develop a predetermined emf at certain temperatures. In this process, the standard value to which the manufacturer has always worked is 36.20 millivolts (abbreviated hereafter mv) when one junction of the thermocouple is at 32° F and the other at 1,600° F.

III. TEST METHODS

In addition to determining the temperature-emf relation for chromel P against alumel, similar relations were also determined for each element against pure platinum. All the thermal-emf values of the individual elements were referred to the platinum standard, Pt 27, maintained at the National Bureau of Standards. This platinum standard is spectroscopically pure and has been thoroughly annealed, and although it may not be the purest platinum that has been or will

[1] BS J. Research **10**, 275 (1933) RP530.

be prepared, it has served as a satisfactory arbitrary standard against which the thermal emf of other materials may be measured. The platinum working standards used in this investigation were checked against the standard Pt 27 before and after the calibration of each of the chromel-alumel thermocouples. The thermal emf of the working platinum standards did not change more than the uncertainty of the measurements (about 2 μv) during any series of measurements. The accuracy of the measurements of chromel P and of alumel against platinum does not in any way affect the results obtained for chromel P against alumel. The sum of the values of thermal emf for chromel P against any material (A) and of alumel against the same material (A) must equal the value for chromel P against alumel, and as all three were measured in this work any two serve as a check upon the third.

The chromel P and alumel wires, insulated by 2-hole porcelain insulators, and the platinum wire, protected by a glazed porcelain tube, were all welded together at the hot junction. The platinum wire was sealed through the end of the protection tube with a pyrex glass, leaving about 1 cm of the platinum wire between the seal and the welded junction.

In the temperature range 0° F to room temperature, the thermocouples were calibrated by comparison with mercury-in-glass standard thermometers in a stirred liquid bath cooled by a carbon-dioxide refrigerating system. In the range room temperature to 1,000° F, the thermocouples were calibrated by comparison with a standard platinum-resistance thermometer. The thermometer and thermocouple were placed to the same depth in holes drilled in an insulated copper block which was heated electrically. The couples were then calibrated in the range 500 to 2,500° F by comparison with standard platinum to platinum-10 percent rhodium thermocouples in a platinum-wound porcelain-tube furnace, 60 cm long and 2.5 cm in diameter. The standard thermocouple wires were insulated with a 2-hole porcelain tube inside a glazed porcelain protection tube. The hot junction end of the thermocouple was sealed through the end of the protection tube with a pyrex glass, leaving about 2 mm of the thermocouple protruding. The hot junction of the platinum-rhodium thermocouple was inserted in a hole about 1.5 mm in diameter, drilled in the hot junction formed by welding the chromel P, alumel and platinum wires.

In all the comparisons with the various types of standards, the cold junctions were maintained at 32° F and the depth of immersion of the chromel-alumel thermocouples in the bath or furnace was 30 cm. All the emf measurements were made with potentiometers. During an observation, the temperature of the bath or furnace was maintained practically constant and the standards were read before and after the observations of the emf of the chromel P vs alumel, chromel P vs platinum and alumel vs platinum. The first thermocouple was calibrated at intervals of 10° in the range 0 to 100° F, 20° in the range 100 to 600° F, 50° in the range 600 to 1,000° F, and 100° above 1,000° F. It was then easily shown that the curves were sufficiently smooth that the accuracy required could be obtained by calibration at intervals of 50° in the range 0 to 1,000° F and of 100°

above 1,000° F. Observations were therefore taken on the remaining thermocouples only at these temperature intervals.

The mercury-in-glass and platinum-resistance thermometers and the platinum-rhodium thermocouples used as standards were either calibrated in accordance with the specifications of the International Temperature Scale [2] or by comparison with other instruments which had been so calibrated. It is estimated that the accuracy of the measurements and the intervals between observation points were such that the uncertainty in the determination of the corresponding values of temperature and emf for each of the 15 couples does not exceed 0.5° in the range 0 to 500° F, 1° in the range 500 to 1,000° F, 2° in the range 1,000 to 2,000° F, and 4° above 2,000° F.

IV. RESULTS

Most of the chromel P wire produced gives 28.50±0.10 mv against platinum when one junction is at 32° F and the other at 1,600° F. Similarly most of the alumel wire gives −7.70±0.10 mv against platinum when the junctions are at 32° F and 1,600° F. As mechanical working and small changes in the chemical composition have an appreciable effect upon the thermal emf, it is difficult to control all of the final product to these limits, particularly the wires of the smaller diameters. In the event that all the wire does not fall within the above limits, the chromel P wire giving 28.30±0.10 mv is combined with alumel giving −7.90±0.10 mv and the chromel P wire 28.70 ±0.10 mv is combined with alumel giving −7.50±0.10 mv. In any case the completed thermocouple gives 36.20±0.20 mv when one junction is at 32° F and the other at 1,600° F. The differences between the shapes of the temperature-emf curves of the thermocouples made by matching the various elements in this way are small compared to the limits within which the manufacturer guarantees to reproduce the standard temperature-emf values. For example, a sample of chromel giving 28.40 mv against platinum when combined with a sample of alumel giving −7.80 mv gives practically the same temperature-emf values as a sample of chromel giving 28.60 mv against platinum when combined with a sample of alumel giving −7.60 mv. The temperature-emf values for two such thermocouples are given in table 1.

TABLE 1.—*Comparison of two chromel-alumel thermocouples*

Temperature °F	Electromotive force					
	Chromel 130 vs Pt	Chromel 171 vs Pt	Alumel 86 vs Pt	Alumel 4620 vs Pt	Chromel 130 vs alumel 86	Chromel 171 vs alumel 4620
	mv	mv	mv	mv	mv	mv
32	0.00	0.00	0.00	0.00	0.00	0.00
500	7.95	8.00	−2.62	−2.58	10.57	10.58
1,000	17.45	17.53	−4.81	−4.71	22.26	22.24
1,600	28.42	28.60	−7.78	−7.60	36.20	36.20
2,000	35.26	35.50	−9.61	−9.38	44.87	44.88
2,500	43.15	43.46	−11.66	−11.34	54.81	54.80

[2] BS J. Research **1**, 635 (1928) RP22.

Of the 15 thermocouples calibrated, 11 were made of chromel P giving 28.50 ± 0.10 mv and of alumel giving -7.70 ± 0.10 mv against platinum at 1,600° F. The other 4 thermocouples were made up of samples giving the following emf against platinum at 1,600° F: 28.82 and −7.38, 28.77 and −7.42, 28.29 and −7.82, and 28.21 and −7.82.

In establishing the temperature-emf relation which is representative of the product now being supplied by the manufacturer, it makes very little difference whether the average of the results obtained on only the 11 thermocouples made of samples giving 28.50 ± 0.10 and $-.7.70 \pm 0.10$ mv against platinum at 1,600° F is used or whether the average of the results obtained on all the samples calibrated is used. The maximum difference would be less than 0.01 mv (0.5° F).

The calibrations of the 11 thermocouples were averaged, giving values of the emf at various temperatures. The average emf at 1,600° F was 36.206 mv. Since all the previous tables issued by the manufacturer of chromel-alumel thermocouples have contained the value 36.20 mv at 1,600° F, this value was retained in the present table. The average values of the emf at the other temperatures were decreased by amounts equal to $e \times \frac{0.006}{36.20}$. This correction factor of 0.006 mv at 1,600° F is equivalent to about 0.3° F. The corrected values of the emf at the various temperatures were then used as the basis for tables 2 and 3. These tables give the temperature-emf equivalents for chromel-alumel thermocouples in degrees Fahrenheit and in degrees centigrade at 10° intervals. The values between the observed points were obtained by interpolation.

The fact that the individual couples were calibrated with an accuracy of from 0.5 to 4° F and that the difference between the calibrations given in table 1 is 1° F or less, does not mean that all chromel-alumel thermocouples will give the temperature-emf relation in table 2 or 3 to this accuracy. The manufacturer guarantees only that the couples give these values within the following limits, ±5° F in the range 32 to 660° F and to ±¾ percent between 660 and 2,300° F. All the couples calibrated in this investigation gave the temperature-emf values in tables 2 and 3 within these guaranteed limits.

The data available indicate that the temperature-emf values in tables 2 and 3 also apply for other sizes of wire. Data were obtained on no. 28 gage wire in the present work and on other sizes from a large number of routine calibrations made at this Bureau over a period of years. However, in the cases of nos. 22 and 28 gage thermocouple wire, the manufacturer's guarantee extends only to 1,600° F, while for no. 18 gage and larger, it extends to 2,000° F, and for no. 11 and larger to 2,300° F.

The difference curves constructed by plotting the emf vs the differences between the calibrations of the individual couples and values in table 2 or 3 approximated straight lines for most of the couples composed of elements giving 28.50 ± 0.10 and -7.70 ± 0.10 mv against platinum at 1,600° F. The curve giving the difference between the calibration of any of the thermocouples and values in tables 2 and 3 is completely determined by calibration at 1,000, 1,600, and 2,000° F.

TABLE 2.—*Standard Fahrenheit table for chromel-alumel thermocouples*

Temperature °F	Electromotive force in millivolts (reference junction at 32° F)										
	0	10	20	30	40	50	60	70	80	90	100
0	−0.68	−0.47	−0.26	−0.04	+0.18	0.40	0.62	0.84	1.06	1.29	1.52
100	1.52	1.74	1.97	2.20	2.43	2.66	2.89	3.12	3.36	3.59	3.82
200	3.82	4.05	4.28	4.51	4.74	4.97	5.19	5.42	5.64	5.87	6.09
300	6.09	6.31	6.53	6.75	6.98	7.20	7.42	7.64	7.87	8.09	8.31
400	8.31	8.53	8.76	8.98	9.20	9.43	9.66	9.88	10.11	10.33	10.56
500	10.56	10.79	11.02	11.25	11.47	11.70	11.93	12.16	12.39	12.62	12.85
600	12.85	13.08	13.31	13.55	13.78	14.01	14.24	14.48	14.71	14.94	15.18
700	15.18	15.41	15.64	15.88	16.11	16.35	16.58	16.82	17.05	17.29	17.52
800	17.52	17.75	17.99	18.22	18.46	18.70	18.93	19.17	19.41	19.64	19.88
900	19.88	20.12	20.36	20.59	20.83	21.07	21.30	21.54	21.78	22.01	22.25
1,000	22.25	22.49	22.72	22.96	23.20	23.43	23.67	23.91	24.14	24.38	24.62
1,100	24.62	24.85	25.09	25.33	25.57	25.80	26.04	26.27	26.51	26.74	26.98
1,200	26.98	27.21	27.45	27.68	27.92	28.15	28.39	28.62	28.86	29.09	29.33
1,300	29.33	29.56	29.79	30.02	30.26	30.49	30.72	30.96	31.19	31.42	31.65
1,400	31.65	31.88	32.11	32.34	32.57	32.80	33.03	33.26	33.49	33.71	33.94
1,500	33.94	34.17	34.40	34.62	34.85	35.08	35.30	35.53	35.75	35.98	36.20
1,600	36.20	36.42	36.65	36.87	37.10	37.32	37.54	37.76	37.99	38.21	38.43
1,700	38.43	38.65	38.87	39.09	39.31	39.53	39.75	39.96	40.18	40.40	40.62
1,800	40.62	40.83	41.05	41.27	41.48	41.70	41.91	42.13	42.34	42.56	42.77
1,900	42.77	42.98	43.20	43.41	43.62	43.83	44.04	44.26	44.47	44.68	44.89
2,000	44.89	45.10	45.31	45.52	45.73	45.93	46.14	46.35	46.56	46.76	46.97
2,100	46.97	47.18	47.38	47.59	47.79	47.99	48.20	48.40	48.61	48.81	49.01
2,200	49.01	49.21	49.41	49.61	49.81	50.01	50.21	50.41	50.61	50.80	51.00
2,300	51.00	51.20	51.39	51.59	51.78	51.98	52.17	52.37	52.56	52.75	52.95
2,400	52.95	53.14	53.33	53.52	53.71	53.90	54.09	54.28	54.47	54.66	54.85
2,500	54.85										

TABLE 3.—*Standard centigrade table for chromel-alumel thermocouples*

Temperature °C	Electromotive force in millivolts (reference junction at 0° C)										
	0	10	20	30	40	50	60	70	80	90	100
0	0.00	0.40	0.80	1.20	1.61	2.02	2.43	2.85	3.26	3.68	4.10
100	4.10	4.51	4.92	5.33	5.73	6.13	6.53	6.93	7.33	7.73	8.13
200	8.13	8.53	8.93	9.34	9.74	10.15	10.56	10.97	11.38	11.80	12.21
300	12.21	12.62	13.04	13.45	13.87	14.29	14.71	15.13	15.55	15.97	16.39
400	16.39	16.82	17.24	17.66	18.08	18.50	18.92	19.36	19.78	20.21	20.64
500	20.64	21.07	21.49	21.92	22.34	22.77	23.20	23.62	24.05	24.48	24.90
600	24.90	25.33	25.75	26.18	26.60	27.03	27.45	27.87	28.29	28.72	29.14
700	29.14	29.56	29.98	30.40	30.82	31.23	31.65	32.07	32.48	32.90	33.31
800	33.31	33.71	34.12	34.53	34.94	35.35	35.75	36.16	36.56	36.96	37.36
900	37.36	37.76	38.16	38.56	38.96	39.35	39.75	40.14	40.53	40.92	41.31
1,000	41.31	41.70	42.08	42.47	42.86	43.24	43.62	44.00	44.38	44.76	45.14
1,100	45.14	45.52	45.89	46.27	46.64	47.01	47.38	47.75	48.12	48.48	48.85
1,200	48.85	49.21	49.57	49.94	50.29	50.65	51.00	51.36	51.71	52.06	52.41
1,300	52.41	52.75	53.10	53.45	53.79	54.13	54.47	54.81	55.15	55.48	55.81
1,400	55.81										

It is believed that the values given in tables 2 and 3 are more representative than any that have been previously published for chromel-alumel thermocouples. These tables make possible more accurate temperature measurements with these thermocouples. The thermocouple alloys and their characteristics have not been changed, and consequently the scales and charts now in use can be used with the same accuracy as in the past.

Tables 4 and 5 giving the emf of chromel P vs platinum and alumel vs platinum were prepared in a similar manner using the data on the same samples as used in preparing tables 2 and 3. The average

value of emf for the chromel P samples against platinum was corrected so as to give 28.50 mv at 1,600° F, and that for alumel against platinum corrected so as to give −7.70 mv at 1,600° F. Only the emf values at every 100° F and every 50° C are given here.

TABLE 4.—*Thermal* emf *of chromel* P *and of alumel* vs *platinum*

Temperature	Electromotive force (reference junction at 32° F)		Temperature	Electromotive force (reference junction 32° F)	
	Chromel P-platinum	Alumel-platinum		Chromel P-platinum	Alumel-platinum
°F	*Millivolts*	*Millivolts*	°F	*Millivolts*	*Millivolts*
0	−0.44	+0.24	1,500	26.73	−7.21
100	1.01	−.51	1,600	28.50	−7.70
200	2.61	−1.21	1,700	30.25	−8.18
300	4.32	−1.77	1,800	31.98	−8.64
400	6.11	−2.20	1,900	33.68	−9.09
500	7.96	−2.60	2,000	35.36	−9.53
600	9.85	−3.00	2,100	37.01	−9.96
700	11.76	−3.42	2,200	38.64	−10.37
800	13.67	−3.85	2,300	40.23	−10.77
900	15.59	−4.29	2,400	41.78	−11.17
1,000	17.50	−4.75	2,500	43.28	−11.57
1,100	19.39	−5.23			
1,200	21.26	−5.72			
1,300	23.11	−6.22			
1,400	24.93	−6.72			

TABLE 5.—*Thermal* emf *of chromel* P *and of alumel* vs *platinum*

Temperature	Electromotive force (reference junction at 0° C)		Temperature	Electromotive force (reference junction at 0° C)	
	Chromel P-platinum	Alumel-platinum		Chromel P-platinum	Alumel-platinum
°C	*Millivolts*	*Millivolts*	°C	*Millivolts*	*Millivolts*
0	0.00	0.00	750	24.60	−6.63
50	1.35	−.67	800	26.23	−7.08
100	2.81	−1.29	850	27.83	−7.52
150	4.35	−1.78	900	29.41	−7.95
200	5.96	−2.17	950	30.98	−8.37
250	7.62	−2.53	1,000	32.52	−8.79
300	9.32	−2.89	1,050	34.05	−9.19
350	11.03	−3.26	1,100	35.56	−9.58
400	12.75	−3.64	1,150	37.05	−9.96
450	14.47	−4.03	1,200	38.51	−10.34
500	16.21	−4.43	1,250	39.95	−10.70
550	17.92	−4.85	1,300	41.35	−11.06
600	19.62	−5.28	1,350	42.71	−11.42
650	21.30	−5.73	1,400	44.04	−11.77
700	22.96	−6.18			

Tables 6 and 7 give the emf of chromel-alumel, chromel-platinum, and alumel-platinum at temperatures below 0°. Only two samples each of chromel P and alumel were used in determining these tables. The samples were taken from lots of wire giving 28.50 and −7.70 mv against platinum at 1,600° F. The values of emf of the thermocouples and those of the individual elements against platinum were

determined by calibration [3] in a stirred liquid bath [4] cooled by liquid air. A platinum-resistance thermometer was used as a standard for determining the temperature.

TABLE 6.—*Thermal* emf *of chromel* P-*alumel, chromel* P-*platinum, and alumel-platinum at low temperatures*

Temperature	Electromotive force (reference junctions at 32° F)			Temperature	Electromotive force (reference junctions at 32° F)		
	Chromel P-alumel	Chromel P-platinum	Alumel-platinum		Chromel P-alumel	Chromel P-platinum	Alumel-platinum
°F	*Millivolts*	*Millivolts*	*Millivolts*	°F	*Millivolts*	*Millivolts*	*Millivolts*
0	−0.68	−0.44	0.24	−160	−3.68		
−10	−.89			−170	−3.84		
−20	−1.10			−180	−4.00		
−30	−1.30			−190	−4.15		
−40	−1.50						
				−200	−4.29	−2.67	1.62
−50	−1.70	−1.10	.60	−210	−4.43		
−60	−1.90			−220	−4.57		
−70	−2.09			−230	−4.71		
−80	−2.28			−240	−4.84		
−90	−2.47						
				−250	−4.96	−3.03	1.93
−100	−2.65	−1.69	.96	−260	−5.08		
−110	−2.83			−270	−5.19		
−120	−3.01			−280	−5.30		
−130	−3.19			−290	−5.41		
−140	−3.36						
				−300	−5.51	−3.28	2.23
−150	−3.52	−2.22	1.30	−310	−5.60		

TABLE 7.—*Thermal* emf *of chromel* P-*alumel, chromel* P-*platinum, and alumel-platinum at low temperatures*

Temperature	Electromotive force (reference junctions at 0° C)			Temperature	Electromotive force (reference junctions at 0° C)		
	Chromel P-alumel	Chromel P-platinum	Alumel-platinum		Chromel P-alumel	Chromel P-platinum	Alumel-platinum
°C	*Millivolts*	*Millivolts*	*Millivolts*	°C	*Millivolts*	*Millivolts*	*Millivolts*
0	0	0	0	−110	−3.78		
−10	−.39			−120	−4.05		
−20	−.77			−130	−4.32		
−30	−1.14			−140	−4.57		
−40	−1.50						
				−150	−4.81	−2.95	1.86
−50	−1.86	−1.20	.66	−160	−5.03		
−60	−2.21			−170	−5.24		
−70	−2.55			−180	−5.43		
−80	−2.87			−190	−5.60		
−90	−3.19						
				−200	−5.75	−3.36	2.39
−100	−3.49	−2.20	1.29				

[3] Acknowledgment is made to D. O. Burger for making these calibrations.
[4] BS J. Research **6**, 401 (1931) RP284.

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METHODS OF TESTING THERMOCOUPLES AND THERMOCOUPLE MATERIALS

By Wm. F. Roeser and H. T. Wensel

ABSTRACT

This paper describes various methods used for testing thermocouples and thermocouple materials, and the precautions which must be observed in order to attain various degrees of accuracy. In particular, it describes in detail the methods developed and used at the National Bureau of Standards. It also provides some guidance to the reader in the selection of the method which is best adapted to a given set of conditions.

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I. INTRODUCTION

Methods of testing thermocouples and thermocouple materials have been developed to supply the need of those industries to which the measurement and control of temperature are essential. The recognition by the various industries in this country that the measurement and control of these temperatures are essential to a uniformly high quality of product has led, in recent years, to a tremendous increase in the use of temperature-measuring equipment. Where the higher temperatures are involved by far the large portion of such measurements are made with thermocouples, and therefore these devices must be regarded as one of the important tools of modern industry.

The users of thermoelectric pyrometers have been demanding ever-increasing accuracy in these instruments. Thermocouple materials are being bought on closer specifications and the pyrometer manufacturers have been setting up smaller tolerances in the inspection and calibration of their product, with the result that practically all pyrometric equipment now being sold is of very high quality. Reliable methods of testing thermocouples and thermocouple materials are required to realize the degree of accuracy now demanded. The purpose of this paper is to describe the more important of these methods and to point out certain precautions that must be observed to secure reliable results. The essential features of many of these methods and much of the apparatus described here have been devised and described in whole or in part by various writers, but references to their papers will be made only when it is felt that a more detailed description than we have given will be helpful to the reader.

Combinations of metals and alloys extensively used in thermocouples for the measurement of temperatures in this country are listed in table 1, together with the temperature ranges in which they are generally used and the maximum temperatures at which they can be used for short periods. The period of usefulness at high temperatures depends largely upon the temperature and the diameter of the wires. The methods described in this paper were devised primarily for calibrating couples in the usual temperature ranges, but unless otherwise indicated they may be used up to the maximum temperatures at which the various types of couples can be used.

TABLE 1.—*Types of thermocouples and temperature ranges in which they are used*

Type of thermocouple	Usual temperature ranges		Maximum temperatures	
	°C	°F	°C	°F
Platinum-rhodium	0 to 1,450	0 to 2,650	1,700	3,100
Chromel-alumel	−200 to 1,200	−300 to 2,200	1,350	2,450
Iron-constantan	−200 to 750	−300 to 1,400	1,000	1,800
Copper-constantan	−200 to 300	−300 to 570	600	1,100

II. GENERAL CONSIDERATIONS

1. TEMPERATURE SCALE

The object in the calibration of any thermocouple is to determine an emf-temperature relation in which the temperature is expressed on a definite and reproducible scale. The International Temperature Scale,[1] adopted in 1927 by thirty-one nations, is now in practically universal use. The methods of realizing this scale are described in detail in the reference cited. The instruments, calibration points, and interpolation equations to be used in the various ranges of the scale are summarized in table 2.

2. GENERAL METHODS

In order to calibrate thermocouples to yield temperatures on the International Scale, it is apparent from the definition that they must be so calibrated that their indications agree with those of the platinum-resistance thermometer in the range −190 to 660° C, the platinum-10 percent rhodium thermocouple in the range 660 to 1,063° C, and the optical pyrometer above 1,063° C. The most direct procedure would therefore be to compare the couples directly with these primary instruments in the appropriate temperature ranges. However, to follow such a procedure in the calibration of every couple requires more time and apparatus than is justifiable or necessary since, in most cases, other methods are available which yield results sufficiently accurate. For example, a thermocouple may be compared indirectly with any of the primary instruments by determining its emf at a number of fixed points, either those which are used in defining the scale or others, the values for which have been determined with the primary instruments. If a few laboratories maintain the apparatus necessary to calibrate thermocouples as working standards to yield temperatures on the International Scale, these standards may be used subsequently to calibrate other couples. This procedure is used far more than any other because the comparison of the indications of two couples is usually simpler than the comparison of two different types of instruments.

The temperature-emf relation of a homogeneous [2] thermocouple is a definite physical property and therefore does not depend upon the details of the apparatus or method employed in determining this relation. Consequently, there are innumerable methods of calibrating thermocouples, the choice of which depends upon the type of couple, temperature range, accuracy required, size of wires, apparatus available, and personal preference.

[1] George K. Burgess. BS J. Research **1**, 635 (1928) RP22.

[2] A homogeneous thermocouple is one in which each element is homogeneous, in both chemical composition and physical condition, throughout its length.

TABLE 2.—*Instruments, calibration points, and interpolation equations of International Temperature Scale*

Temperature ranges		Instruments	Calibration points (values for pressure of one standard atmosphere)			Interpolation equations [a]
°C	°F		*Fixed point*	°C	°F	
−190 to 0	−310 to 32	Platinum resistance thermometer	Boiling point of oxygen	−182.97	−297.35	$R_t = R_0[1+At+Bt^2+C(t-100)t^3]$
			Melting point of ice	0.000	32.000	
			Boiling point of water	100.000	212.000	
			Boiling point of sulphur	444.60	832.28	
0 to 660	32 to 1,220	Platinum resistance thermometer	Melting point of ice	0.000	32.000	$R_t = R_0(1+At+Bt^2)$
			Boiling point of water	100.000	212.000	
			Boiling point of sulphur	444.60	832.28	
660 to 1,063	1,220 to 1,945	Platinum to platinum-10 percent rhodium thermocouple.	Freezing point of antimony	(630.5) [b]	(1,166.9)	$e = a+bt+ct^2$
			Freezing point of silver	960.5	1,760.9	
			Freezing point of gold	1,063.0	1,945.4	
1,063 and above	1,945 and above	Optical pyrometer	Freezing point of gold	1,063.0	1,945.4	$\log_e \frac{J_\lambda}{J_1} = \frac{C_2}{\lambda}\left(\frac{1}{1,336} - \frac{1}{t+273}\right)$

[a] R_t is the resistance at $t°$ C, R_0, the resistance at 0° C; A and B are constants determined by calibration at the boiling points of water and sulphur, and C is an additional constant determined by calibration at the boiling point of oxygen. e is the emf at $t°$ C and a, b, and c are constants. J_λ is the monochromatic visible radiation at wave length λ cm emitted by a black body at temperature $t°$ C, J_1 the radiation of the same wave length emitted by a black body at the gold point, and C_2 is 1.432 cm degrees.

[b] The value for the freezing point of the particular lot of antimony used is determined by means of the platinum-resistance thermometer.

Thermocouple calibrations are required with various degrees of accuracy ranging from 0.01 to 10 or 20° C. For an accuracy of 0.1° C agreement with the International Temperature Scale and methods of interpolating between the calibration points become problems of prime importance, but for an accuracy of about 10° C comparatively simple methods of calibration will usually suffice. The most accurate calibrations in the range −190 to 300° C are made by comparing the couples directly with a standard platinum-resistance thermometer in a stirred liquid bath. In the range 300 to 660° C (and below if a platinum-resistance thermometer or stirred liquid bath is not available) couples are most accurately calibrated at the freezing or boiling points of pure substances. Between 660 and 1,063° C, the platinum-10 percent rhodium thermocouple calibrated at the freezing points of gold, silver, and antimony, serves to define the International Temperature Scale and other types of couples are most accurately calibrated in this range by direct comparison with the standard couple calibrated as specified. Other couples may be calibrated just as accurately at the fixed points as the 10-percent rhodium couple, but interpolated values at intermediate points may depart slightly from the International Scale. Above 1,063° C, the most basic calibrations are made by observing the emf when one junction of the couple is in a blackbody furnace, the temperature of which is measured with an optical pyrometer. However, the difficulties encountered in bringing a blackbody furnace to a uniform temperature make the direct comparison of these two types of instruments by no means a simple matter. Other methods of calibrating a couple above 1,063° C are given under melting points and under methods of interpolation.

Although the 10-percent rhodium couple serves to define the scale only in the range 660 to 1,063° C, this type of couple calibrated at fixed points is used extensively both above and below this range as a working standard in the calibration of other thermocouples. For most industrial purposes a calibration accurate to 2 or 3° C in the range room temperature to 1,200° C is sufficient. Other couples can be calibrated by comparison with such working standards almost as accurately as the calibration of the standard is known. However, it might be pointed out that outside the range 660 to 1,063° C any type of couple suitable for the purpose, and calibrated to agree with the resistance thermometer or optical pyrometer in their respective ranges, has as much claim to yielding temperatures on the International Scale as the platinum-10 percent rhodium couple. In fact, at the lower temperatures certain types of base-metal couples are definitely better adapted for precise measurements.

The calibration of couples then may be divided into two general classes, depending upon the method of determining the temperature of the measuring junction, (1) calibration at fixed points and (2) calibration by comparison with standard instruments such as thermocouples, resistance thermometers, etc.

In order to obtain the high accuracies referred to above and usually associated with calibrations at fixed points, it is necessary to follow certain prescribed methods and to take the special precautions described in detail in the following sections, but for an accuracy of about 5° C the more elaborate apparatus to be described need not be employed.

3. HOMOGENEITY

The magnitude of the emf developed by a couple depends upon the composition of the wires in the region of temperature gradients. The emf developed by an inhomogeneous couple is characteristic of the temperature of the hot junction only when the region of inhomogeneity is not in a region of temperature gradients. Therefore, in order to obtain a high degree of accuracy with a couple, the homogeneity of the wires must be established.

Thermocouple wire now being produced by the wire manufacturers in this country is sufficiently homogeneous in chemical composition for most purposes. Occasionally inhomogeneity in a couple may be traced to the manufacturer, but such cases are rare. More often it is introduced in the wires during tests or use. It usually is not necessary, therefore, to examine new thermocouples for inhomogeneity, but thermocouples that have been used for some time should be so examined before an accurate calibration is attempted.

While rather simple methods are available for detecting thermoelectric inhomogeneity, no satisfactory method has been devised for quantitatively determining it or the resulting errors in the measurement of temperatures. Abrupt changes in the thermoelectric power may be detected by connecting the two ends of the wire to a sensitive galvanometer and slowly moving a source of heat, such as a bunsen burner or small electric furnace, along the wire. This method is not satisfactory for detecting gradual changes in the thermoelectric power along the length of the wire. Inhomogeneity of this nature may be detected by doubling the wire and inserting it to various depths in a uniformily heated furnace, the two ends of the wire being connected to a galvanometer as before. If, for example, the doubled end of the wire is immersed 25 cm in a furnace with a sharp temperature gradient so that two points on the wire 50 cm apart are in the temperature gradient, the emf determined with the galvanometer is a measure of the difference in the thermoelectric properties of the wire at these two points.

After reasonable homogeneity of one sample of wire has been established, it may be used in testing the homogeneity of similar wires by welding the two together and inserting the junction into a heated furnace. The resulting emf at various depths of immersion may be measured by any convenient method. Other similar methods have been described for detecting inhomogeneity.[3]

Tests such as those described above will indicate the uncertainty in temperature measurements due to inhomogeneity in the wires. For example, if a difference in emf of 10 microvolts (abbreviated hereafter μv) is detected along either element of a platinum-rhodium couple by heating various parts of the wire to 600° C, measurements made with it are subject to an uncertainty of the order of 1° at 600° C or of 2° at 1,200 ° C. Similarly, if an emf of 10 μv is detected along an element of a base-metal couple with a source of heat at 100° C, measurements made with it are subject to an uncertainty of the order of 0.2° C at this temperature. The effects of inhomogeneity in both wires may be either additive or subtractive and, as the emf developed

[3] W. P. White, Phys. Rev. **23**, 449 (1906); **31**, 135 (1910). J. Am. Chem. Soc. **36**, 2292 (1914). Foote, Fairchild, and Harrison. Tech. Pap. BS **14** (1920-21) T170.

along an inhomogeneous wire depends upon the temperature distribution, it is evident that corrections for inhomogeneity are impracticable if not impossible.

4. ANNEALING

Practically all base-metal thermocouple wire produced in this country is annealed or given a "stabilizing heat treatment" by the manufacturer. Such treatment is generally considered sufficient, and seldom is it found advisable to further anneal the wire before testing.

Although the new platinum-rhodium thermocouple wire as sold by some manufacturers is already annealed, it has become regular practice in many laboratories to anneal or "stabilize" all platinum-rhodium couples, whether new or previously used, before attempting an accurate calibration. This is usually accomplished by heating the wire electrically in air. The entire length of wire is supported between two binding posts, which should be close together so that the tension in the wires and stretching while hot are kept at a minimum. The temperature of the wire is most conveniently determined with an optical pyrometer.[4] It is necessary, however, to add a correction to the observed apparent temperature to obtain the true temperature, which is always the higher. The correction (based on an emissivity of 0.33) amounts to 130 and 145° C, respectively, for apparent temperatures of 1,270 and 1,350° C.

There is some question as to the optimum temperature or length of time at which such couples should be annealed to produce the most constant characteristics in later use. As a matter of fact, there is some question as to whether annealing for more than a few minutes is harmful or beneficial. Most of the mechanical strains are relieved during the first few minutes of heating at 1,400 to 1,500° C, but it has been claimed that the changes in the thermal emf of a couple in later use will be smaller if the wires are heated for several hours before calibration and use. The principal objection to annealing thermocouples for a long time at high temperatures, aside from the changes in emf taking place, is that the wires are weakened mechanically as a result of crystal growth. During the past ten years the practice at the National Bureau of Standards was to anneal all platinum-rhodium couples electrically for 6 hours at 1,500° C before calibration. The emf of a number of new thermocouples was determined both after annealing for 5 minutes and for 6 hours at 1,500° C and in no case did the change in emf correspond to as much as 2° C at 1,200° C. After 6 hours of heating, the wires, particularly the platinum element, become much softer. It has been found, however, that annealing at temperatures much above 1,500° C produces rapid changes in the emf and leaves the wire very weak mechanically. The National Bureau of Standards on January 2, 1935, adopted the procedure of annealing all platinum-rhodium couples for 1 hour at 1,450° C.

[4] The ordinary portable type of optical pyrometer is very satisfactory for this purpose. As commonly used the magnification is too low for sighting upon an object as small as the wires of rare-metal couples, but this is easily remedied by inserting an additional piece of telescoping tubing so that the objective lens of the pyrometer is about twice as far from the pyrometer lamp as it is when sighting upon distant objects. Such a tube should preferably be made of metal, but one made by simply rolling up a sheet of heavy paper will do very well.

It has not been demonstrated conclusively that platinum-rhodium thermocouples after contamination can be materially improved in homogeneity by prolonged heating in air, although it is logical to suppose that certain impurities can be driven off or, through oxidation, rendered less detrimental.

5. INSTRUMENTS

One of the factors in the accuracy of the calibration of a thermocouple is the accuracy of the instrument used to measure the emf. Fortunately, in most instances, an instrument is available whose performance is such that the accuracy of the calibration need not be limited by the accuracy of the emf measurements. For work of the highest accuracy it is advisable to use a potentiometer of the type designed by Diesselhorst,[5] White,[6] or Wenner,[7] in which there are no slide wires and in which all the settings are made by means of dial switches. However, for most work, in which an accuracy of 5 μv will suffice, slide-wire potentiometers of the laboratory type are sufficiently accurate. Portable potentiometers accurate within 40 to 100 μv are also available. Aside from the greater sensitivity obtained, an important advantage of using a potentiometer is the fact that the reading obtained is independent of the resistance of the couple.

Indicators of the galvanometric type are seldom used in making calibrations. Galvanometer indicators should be graduated for a specified external resistance of couple and leads, and the resistance of the indicator itself should be high in order to minimize the effects of changes in the resistance of the couple and leads. Detailed discussion is given and special instruments used in measuring the emf of thermocouples are described in Bureau of Standards Technologic Paper T170.

III. CALIBRATION AT FIXED POINTS

One of the important applications of the method of calibrating thermocouples at fixed points is found in the calibration of platinum-10-percent rhodium thermocouples to realize the International Temperature Scale in the range 660 to 1,063° C. From such a calibration, together with methods of extrapolation described later, the temperature-emf relation of this type of couple may be determined with an accuracy of about 2° C at 1,500° C. Calibration at a few other selected points below 660° C will yield a working standard which is accurate to a few tenths of a degree in the range 0 to 1,100° C. Fixed points are also conveniently used with various degrees of accuracy ranging from 0.1 to 5° C in the calibration and checking of various types of thermocouples in the range −190° C to the melting point of platinum (1,773° C). The fixed points for which values have been assigned or determined accurately and at which it has been found convenient to calibrate thermocouples are given in table 3. The values in the table apply for a pressure of one standard atmosphere (760 mm of Hg) and the variations of the boiling temperatures with pressure are given in the last column.

[5] H. Diesselhorst, Z. Instrumentenk. **28**, 1 (1908).
[6] W. P. White, Z. Instrumentenk. **27**, 210 (1907).
[7] L. Behr, Rev. Sci. Instruments, **3**, 108 (1932).

TABLE 3.—*Fixed points available for calibrating thermocouples*

Thermometric fixed point	Values on the International Temperature Scale				Temperature of equilibrium (t_p) in °C as a function of the pressure (p) between 680 and 780 mm of Hg
	Assigned (Primary points)		Determined (Secondary points)		
	°C	°F	°C	°F	
Boiling point of oxygen	−182.97	−297.35			$t_p=t_{760}+0.0126(p-760)-0.0000065(p-760)^2$
Sublimation point of carbon dioxide.			−78.5	−109.3	$t_p=t_{760}+0.1443(t_p+273.2)\log\left(\frac{p}{760}\right)$
Freezing point of mercury			−38.87	−37.97	
Melting point of ice	0.000	32.000			
Boiling point of water	100.000	212.000			$t_p=t_{760}+0.0367(p-760)-0.000023(p-760)^2$
Boiling point of naphthalene			217.96	424.33	$t_p=t_{760}+0.208(t_p+273.2)\log\left(\frac{p}{760}\right)$
Freezing point of tin [1]			231.9	449.4	
Boiling point of benzophenone			305.9	582.6	$t_p=t_{760}+0.194(t_p+273.2)\log\left(\frac{p}{760}\right)$
Freezing point of cadmium			320.9	609.6	
Freezing point of lead [1]			327.3$_5$	621.2$_9$	
Freezing point of zinc [1]			419.4$_8$	787.0$_6$	
Boiling point of sulphur	444.60	832.28			$t_p=t_{760}+0.0909(p-760)-0.000048(p-760)^2$
Freezing point of antimony			630.5	1,166.9	
Freezing point of aluminum [1]			660.1$_8$	1,220.2$_7$	
Freezing point of Cu-Ag eutectic alloy.[2]			778.8	1,433.8	
Freezing point of silver	960.5	1,760.9			
Freezing point of gold	1,063.0	1,945.4			
Freezing point of copper [1]			1,083.0	1,981.4	
Melting point of palladium			1,555	2,831	
Melting point of platinum			1,773	3,223	

[1] Standard samples of these materials are procurable from the National Bureau of Standards with certificates giving the freezing point of the particular lot of metal. The values given in this table for these materials apply for the standard samples that are being issued as of the present date.

[2] 28.1 percent copper and 71.9 percent silver by weight.

In selecting the points at which to calibrate a couple, one sometimes has a choice between a boiling or a freezing point,[8] as for example, between the boiling point of sulphur (444.60° C) and the freezing point of zinc (419.48° C), between the boiling point of naphthalene (217.96° C) and the freezing point of tin (231.9° C), or between the boiling point of benzophenone (305.9° C) and the freezing point of cadmium (320.9° C) or lead (327.35° C). In determining the emf of a couple at a freezing point, the time in which observations may be taken is limited to the period of freezing, after which the material must be melted again before taking further observations. In the case of boiling points, there is no such limit in time since the material can be boiled continuously. In addition there is sometimes a question as to the beginning and end of the interval of constant-temperature characteristic of freezing. On the other hand, it is not necessary to observe the pressure during freezing and in general simpler apparatus and less skill are required to obtain a given accuracy with freezing points.

[8] In this paper "boiling point" is used for the temperature of equilibrium between the liquid and vapor phases although the point is usually realized experimentally by immersing the couple in the condensing vapor. "Freezing point" is used for the temperature of equilibrium between the solid and liquid phases when the point is realized experimentally by immersing the couple in the freezing material, and "melting point" is used for the same point when it is realized experimentally by determining the emf of a couple while the material is melting. When conditions permit a choice, freezing points are preferable to melting points of metals because the molten metal can be brought to a uniform temperature just prior to freezing by stirring more easily than the solid can be brought to a uniform temperature just prior to melting, a condition that must be met to obtain accurate results.

1. FREEZING POINTS

The emf developed by a homogeneous thermocouple at the freezing point of a metal is constant and reproducible if all of the following conditions are fulfilled: (1) the couple is protected from contamination; (2) the couple is immersed in the freezing-point sample sufficiently far to eliminate heating or cooling of the junction by heat flow along the wires and protection tube; (3) the reference junctions are maintained at a constant and reproducible temperature; (4) the freezing-point sample is pure; and (5) the metal is maintained at essentially a uniform temperature during freezing. The methods of obtaining these conditions are subject to a choice. However, the essential features of the methods employed at the National Bureau of Standards are described here.

(a) PROTECTION TUBES

Closed-end porcelain or pyrex-glass tubes are generally used to protect thermocouples from contamination, which usually results from the thermocouple wires coming in contact with other metals or metallic vapors or from the action of reducing gases at high temperatures. In the latter case, the silica of the insulating or protecting tube is reduced to silicon which alloys with the thermocouple wires. For temperatures above 600° C the wires should be insulated by porcelain tubing and protected from contamination by a glazed porcelain tube. It is advisable to heat these tubes before use, to about 1,200° C in an oxidizing atmosphere to burn out any carbonaceous material that may have collected in them during storage and shipping. Protection tubes 5 mm inside diameter, 7 mm outside diameter, and 50 cm long are convenient for platinum-rhodium thermocouples insulated by two-hole insulating tubes 50 cm long and 4 mm in diameter with 1 mm holes. For temperatures below 600° C, pyrex tubes are very satisfactory for both protecting and insulating the wires.

(b) DEPTH OF IMMERSION

The depth of the immersion necessary to avoid heating or cooling of the junction by heat flow along the thermocouple wires and protection tube depends upon the material and size of the wires, the dimensions of the insulating and protecting tubes, and the difference between the temperature of the freezing-point sample and that of the furnace and atmosphere immediately above it. The safest method of determining whether the depth of immersion is sufficient is by trial. It should be such that during the period of freezing the thermocouple can be lowered or raised at least 1 cm from its normal position without altering the indicated emf by as much as the allowable uncertainty in the calibration. For platinum-rhodium thermocouples in the protection tube described above, a depth of 10 cm, which is greater than necessary, is used at the National Bureau of Standards.

(c) REFERENCE-JUNCTION TEMPERATURE CONTROL

The temperature of the reference junctions is most easily controlled at a known temperature by placing them in an ice bath. A wide-mouth thermos bottle filled with shaved ice saturated with water is very satisfactory. Electrical connection between a thermocouple wire and a copper lead wire is easily made by inserting them into a

small glass tube containing a few drops of mercury. The glass tubes are then inserted into the ice bath to a depth of about 10 cm. The lead wires should be insulated from the thermocouple wires, except where they make contact through the mercury. The glass tubes should be kept clean and dry inside. Moisture is likely to condense in the tube from the atmosphere but should not be allowed to accumulate. A little moisture and dirt at the bottom of the tube will form a galvanic cell which may vitiate the readings. A later section deals with cold-junction temperatures in general.

(d) PURITY OF FREEZING-POINT SAMPLES

The temperature at which a metal freezes depends upon the amount and kind of impurities present. The values in table 3 apply for metals, the purity of which is of the order of 99.99 percent. The freezing temperature of silver, gold, or copper may be lowered by as much as 0.1° C and that of antimony, aluminum, zinc, lead, cadmium, tin, or mercury by as much as 0.05° C by 0.01 percent of impurities. The purity of the standard-sample freezing-point materials issued by the National Bureau of Standards is not of great importance, as a certificate is issued with each sample giving the freezing temperature determined on that particular lot of metal. However, the purest metals available are selected for these standard samples because a high degree of purity is necessary in order that the metal may give a flat freezing curve.

(e) CRUCIBLES

Of the crucible materials ordinarily used Acheson graphite has the greatest utility and is used almost exclusively at the National Bureau of Standards for this work. It is very pure, can be machined into any desired shape, and can be used in contact with any of the freezing-point materials in table 3 without detectable contamination of the metals. At high temperatures the gases formed from its oxidation provide the reducing atmosphere usually necessary for the protection of the freezing-point metal. Copper and copper oxide form a eutectic which melts about 20° C lower than pure copper, and it is possible for molten silver to absorb enough oxygen from the air to lower its freezing point as much as 10° C. Therefore, copper and silver must be protected from oxygen, and it is advisable also to protect aluminum and antimony from oxygen. This is done by using graphite crucibles with covers of the same material and as an added precaution these freezing-point metals are covered with powdered graphite or charcoal.

Porcelain tubes or crucibles, or any material containing silica cannot be used in contact with aluminum, as the silica is readily attacked. Aluminum is melted in a graphite crucible and the porcelain protecting tube separated from the aluminum by a very thin sheath of graphite. Figure 1 illustrates one convenient manner in which the sheath may be mounted in the crucible. The sheath is held down in the metal by the weight of the cover and is allowed to remain in the crucible after the aluminum is frozen. The thermocouple protecting tube fits snugly inside the sheath. At the National Bureau of Standards the graphite crucibles used for gold, silver, antimony, and zinc are 3 cm inside diameter and 15 cm deep. The

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crucibles used for copper, aluminum, lead, and tin are 5 cm inside diameter and 15 cm deep. Porcelain, silica, clay, clay graphite, and pyrex glass are also used as crucible materials. Pyrex glass is very suitable for mercury.

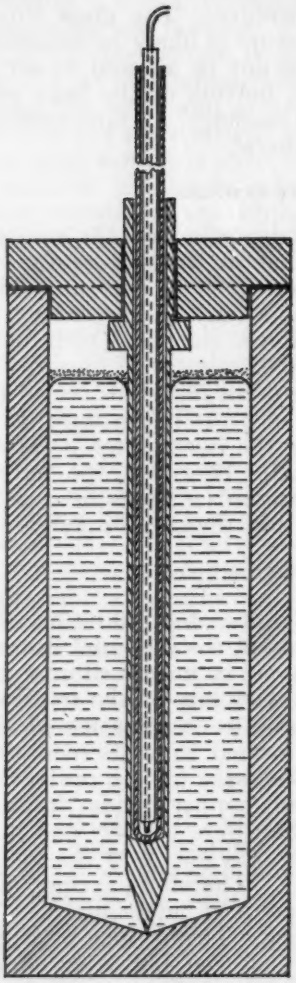

FIGURE 1.—*Arrangement for protecting a thermocouple in molten aluminum.*

(f) FURNACES

Figure 2 shows the type of furnace used in the freezing-point determinations. The heating element is no. 6 or 8 gage nickel(80)-chromium(20) wire wound on an alundum tube and imbedded in alundum cement. The space between the heating element and the outside wall is filled with silocel powder. Acheson-graphite diaphragms are placed above the crucible in order to minimize the oxidation of the crucibles and to promote temperature uniformity in the metal.

(g) PROCEDURE

In the calibration of a thermocouple at freezing points, the couple, properly protected, is slowly immersed in the molten metal. The metal is brought to essentially a uniform temperature at the beginning of freezing by holding its temperature constant at about 10° C above the freezing point for several minutes and then cooling slowly, or by stirring the metal with the thermocouple protection tube just before freezing begins. The emf of the couple is observed at regular intervals of time. These values are plotted and the emf corresponding to the flat portion of the cooling curve is the emf at the freezing point of the metal.

Antimony and tin have a marked tendency to undercool before freezing, but the undercooling will not be excessive if the liquid metal is stirred.

2. MELTING POINTS

The emf of a thermocouple at the melting point of a metal may be obtained in the same manner and with the same apparatus as that just described for freezing points, but the latter are

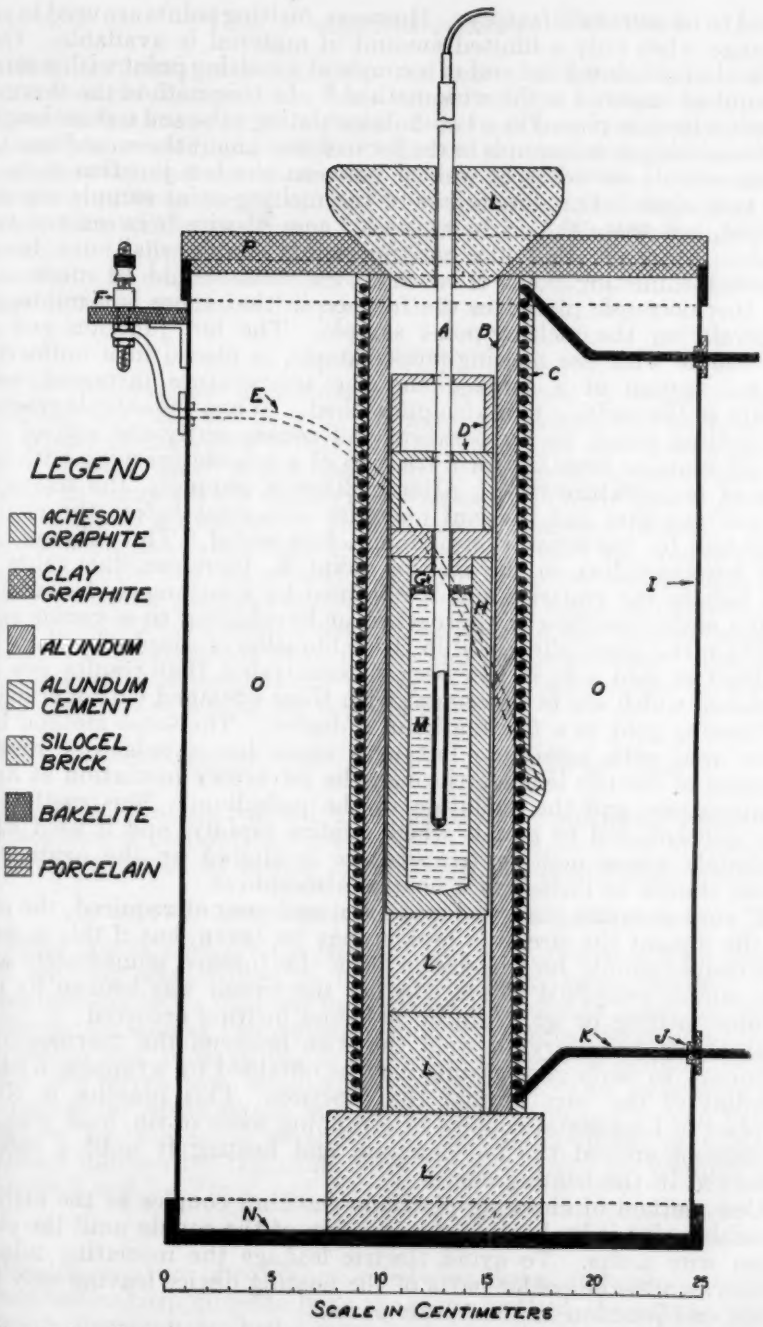

FIGURE 2.—*Furnace used in calibrating couples at freezing points of metal.*

A, porcelain protecting tube; B, alundum furnace tube; C, heating element (80 nickel, 20 chromium); D, graphite diaphragms; E, control thermocouple (chromel-alumel); G, graphite powder; H, graphite crucible; I, sheet steel; M, freezing-point metal; N, cast-iron base; O, silocel-powder insulation.

found to be more satisfactory. However, melting points are used to advantage when only a limited amount of material is available. One method of obtaining the emf of a couple at a melting point with a small amount of material is the wire method.[9] In this method the thermocouple wires are placed in a two-hole insulating tube and a short length of the melting-point sample in the form of wire about the same diameter as the couple elements, is welded between the hot junction ends of the two wires. The dimensions of the melting-point sample are not critical, but there should be at least 1 mm of wire between the two welds. In order that the melting-point sample shall not break before the melting point is reached, the weld should be made and the thermocouple placed in the furnace so that there is a minimum of strain on the melting-point sample. The hot junction end of the couple with the melting-point sample, is placed in a uniformly heated section of a furnace and the temperature increased very slowly as the melting point is approached. When the sample reaches its melting point, its temperature and consequently the emf of the couple remains constant for a fraction of a minute (varying with the rate of temperature rise). After melting is complete, the temperature of the wire and the emf may rise somewhat before the circuit is broken by the separation of the molten metal. The value of the emf corresponding to the melting point is, therefore, the value at the halt in the emf rise and is obtained by continuous observation of the emf as melting is approached or by plotting time versus emf.

The metal most often used in the calibration of couples by the wire method is gold and it has been demonstrated that results can be obtained which are in agreement with those obtained with a crucible of freezing gold to a few tenths of a degree. The same method has been used with palladium but with much less satisfactory results because of electric leakage through the refractory insulation at high temperatures and the oxidation of the palladium. This method is not well adapted to metals which oxidize rapidly, and if used with materials whose melting temperature is altered by the oxide, the metal should be melted in a neutral atmosphere.

If very accurate observations of the emf are not required, the emf at the instant the circuit is broken may be taken, but if this is done the couple should be withdrawn from the furnace immediately and the sample examined to see whether the circuit was broken by the sample melting or by strain on it before melting occurred.

It is not necessary to weld the wire between the thermocouple elements, as fairly good results may be obtained by wrapping a small amount of the wire around the junction. This practice is often applied to base-metal couples by wrapping wires of tin, lead, zinc, or aluminum around the hot junction and heating it until a halt is observed in the heating curve.

One method of checking platinum-rhodium couples at the highest possible point is by heating the junction of the couple until the platinum wire melts. To avoid electric leakage the insulating tube is withdrawn to the colder parts of the heating device leaving only the wires and junction in the hotter parts.

[9] Hoffmann and Meissner Ann. Phys. **60**, 201 (1919). Fr. Hoffmann. Z. Phys. **37**, 285 (1924). Fairchild, Hoover, and Peters. BS J. Research **2**, 931. (1929) RP65.

3. BOILING POINTS

Boiling points play an important part in the definition of the International Temperature Scale, since 3 of the 4 points upon which the scale between −190 and 660° C is based, are the boiling points of oxygen, water, and sulphur. However, boiling points with the exception of that of water, are seldom used in the calibration of thermocouples and consequently the methods of realizing these various points will be mentioned only briefly here. References are given to complete discussions for those interested, as boiling points might profitably be employed to a greater extent, when a platinum-resistance thermometer or a stirred liquid bath is not available.

(a) STEAM POINT

The temperature of condensing water vapor is realized experimentally by the use of a hypsometer so constructed as to avoid superheat of the vapor around the thermocouple and contamination with air and other impurities. Simple types of hypsometers are shown in various trade catalogs. Mueller and Sligh [10] give a detailed description of a hypsometer used in precision measurements. If the proper conditions are attained, the observed emf of the couple will be independent of the rate of heat supply to the boiler, the length of time the hypsometer has been in operation, and the depth of immersion of the couple. The couple for some distance from the junction must be shielded from radiation from hotter and colder surfaces. The relation between the temperature (t_p) in ° C and the pressure (p) for the range 680 to 780 mm of Hg is given by

$$t_p = 100.000 + 0.0367\ (p-760) - 0.000023\ (p-760)^2$$

The steam point as realized by utilizing the condensing vapor in a hypsometer is certainly accurate 0.01° C. An accuracy of about 1° C can be obtained by merely immersing a couple in boiling water.

(b) SULPHUR, BENZOPHENONE, AND NAPHTHALENE POINTS

These points are near the freezing points of available pure metals and are very seldom used in the calibration of thermocouples. The specifications to be followed in realizing the sulphur point are given in the International Temperature Scale.[11] Detailed description of the apparatus and precautions to be observed for the sulphur boiling point are given by Mueller and Burgess.[12] The procedure and apparatus for realizing the boiling points of naphthalene and benzophenone are the same as those for the boiling point of sulphur. Detailed information regarding these points is given by Waidner and Burgess [13] and by Finck and Wilhelm.[14]

(c) OXYGEN POINT

The temperature of equilibrium between liquid and gaseous oxygen is best realized experimentally by the static method, the oxygen vapor-pressure thermometer being compared with the thermocouple to be calibrated in a suitable low-temperature bath. An oxygen vapor-pressure thermometer is nothing more than a glass tube containing

[10] J. Opt. Soc. Am. and Rev. Sci. Inst. **6**, 958 (1922).
[11] BS J. Research **1**, 635 (1928) RP22.
[12] BS Sci. Pap. **15**, 163 (1919-20) S339.
[13] Bul. BS **7**, 1 (1911) S143.
[14] J. Am. Chem. Soc. **47**, 1577 (1925).

very pure oxygen at a pressure of several atmospheres at room temperature, and connected to a mercury-filled manometer for measuring the pressure in the tube. When the thermometer tube is immersed in the bath, part of the oxygen liquefies. The temperature (t_p) in °C of the bath is related to the pressure (p) in the thermometer by $t_p = -182.97 + 0.0126\ (p-760) - 0.0000065\ (p-760)^2$ in the range 680 to 780 mm of Hg. This requires that the temperature of the bath be kept within the limits −183.9 to −182.7° C. This is most conveniently done by stirring liquid oxygen in a dewar flask.

(d) CARBON-DIOXIDE POINT

Although the sublimation point of carbon dioxide is not a boiling point, the highest accuracy is obtained in utilizing this point, by employing the same method as that for the boiling point of oxygen. An instrument of this type suitable for use as a carbon-dioxide vapor-pressure thermometer is container type 3, described by Meyers and Van Dusen.[15] The sublimation point of carbon dioxide may also be utilized by immersing the couple in a slush made by mixing carbon-dioxide snow with a liquid such as acetone. The slush should be stirred and the air excluded from the vapor above the surface of the slush. Whereas the accuracy obtained with a vapor-pressure thermometer is of the order of a few hundredths of a degree, an accuracy of 1° C is all that can be claimed for the temperature of the slush.

IV. CALIBRATION BY COMPARISON METHODS

The calibration of a thermocouple by comparison with a working standard is sufficiently accurate for most purposes and can be done conveniently in most industrial and technical laboratories. The success of this method usually depends upon the ability of the observer to bring the junction of the couple to the same temperature as the actuating element of the standard, such as the hot junction of a standard thermocouple or the bulb of a resistance or liquid-in-glass thermometer. The accuracy obtained is further limited by the accuracy of the standard. Of course, the reference-junction temperature must be known, but this can usually be controlled by using an ice bath as described earlier or measured by a liquid-in-glass thermometer. The method of bringing the junction of the couple to the same temperature as that of the actuating element of the standard depends upon the type of couple, type of standard, and the method of heating.

1. PLATINUM-RHODIUM THERMOCOUPLES

Platinum-rhodium thermocouples, either the 10- or 13-percent rhodium, are seldom used for accurate measurements below 300° C (572° F) and are practically never used below 0° C, because the thermal emf per degree of these couples decreases rapidly at low temperatures, becoming zero at about −138° C (−216° F). These couples are usually calibrated above 300° C by comparison with standard thermocouples in electrically heated furnaces. The standard couple may be either a 10- or 13-percent rhodium couple that has been calibrated at fixed points or by comparison with other couples so calibrated.

[15] BS J. Research **10**, 381 (1933) RP538.

The method employed at the National Bureau of Standards for the comparison of two such couples permits simultaneous reading of the emf of each couple without waiting for the furnace to come to a constant temperature. In order to insure equality of temperature between the measuring junctions of the couples, they are welded together. A separate potentiometer is used to measure each emf, one connected to each thermocouple, and each potentiometer is provided with a reflecting galvanometer. The two spots of light are reflected onto a single scale, the galvanometers being set in such a position that the spots coincide at the zero point on the scale when the circuits are open and therefore also when the potentiometers are set to balance the emf of each thermocouple. Simultaneous readings are obtained by setting one potentiometer to a desired value and adjusting the other so that both spots of light pass across the zero of the scale together as the temperature of the furnace is raised or lowered.

By making observations first with a rising and then with a falling temperature, the rates of rise and fall being approximately equal, and taking the means of the results found, several minor errors such as those due to differences in the periods of the galvanometers, etc., are eliminated or greatly reduced. The differences between the values observed with rising and falling temperatures are usually less than 5μv with platinum-rhodium couples, if the periods of the galvanometers are approximately the same.

This method is particularly adapted to the calibration of couples at any number of selected points. For example, if it is desired to determine the temperature of a couple corresponding to 10.0mv, this emf is set up on the potentiometer connected to this couple, the emf of the standard couple observed as described above, and the temperature obtained from the emf of the standard. If it is desired to determine the emf of a couple corresponding to 1,000° C, the emf of the standard corresponding to this temperature is set up on the potentiometer connected to the standard and the emf of the couple being tested is observed directly.

In order to calibrate a couple in the least possible time by this method, it is necessary to use a furnace that is so constructed that it will cool rapidly. The heating element of the furnace used at the National Bureau of Standards for the routine testing of couples consists of a nickel(80)-chromium(20) tube clamped between two water-cooled terminals. The tube, which is $^{13}/_{16}$ inch inside diameter, $^{15}/_{16}$ inches outside diameter, and 24 inches long, is heated electrically, the tube itself serving as the heating element or resistor. The large current necessary to heat the tube is obtained from a transformer. A large cylindrical shield of sheet metal is mounted around the heating tube to reduce the radiation loss. To minimize lag no thermal insulation is used between the heating tube and the radiation shield. The middle part of this furnace for about 18 inches is at practically a uniform temperature and the water-cooled terminals produce a very sharp temperature gradient at each end. This furnace can be heated to 1,200° C in about 5 minutes with 12 kw and, if all the power is shut off, will cool from this temperature to 300° C in about the same time. This type of furnace can be used up to 1,250° C (2,282° F).

The thermocouples are insulated and protected by porcelain tubes. It is essential that the two potentiometers and thermocouple circuits be separate except at the point where the junctions are welded together. The cold junctions are maintained at 0° C.

The above method and apparatus were devised primarily for the rapid testing of couples, but it is not necessary to follow this method literally or to procure identical apparatus to obtain good results. If it is not convenient to weld the junctions of the couples together, they may be brought into fairly good contact by wrapping with platinum wire or foil. The only advantage of the furnace described above, over any other type of furnace in which several inches of the couples may be heated to a uniform temperature, is the flexibility of control. Electric tube furnaces suitable for such comparison tests can be obtained, designed to operate on either 110 or 220 v, and may be obtained equipped with an adjustable rheostat for regulating the current. For temperatures up to 1,150° C (2,102° F), a furnace with a heating element of nickel(80)-chromium(20) will suffice. Furnaces with heating elements of platinum or platinum-rhodium are available for higher temperatures. A convenient size of heating tube is 1 inch in diameter and 18 inches long. Even though the furnace tube is kept fairly clean, it is advisable to protect platinum-rhodium couples by a porcelain tube. If two potentiometers are not available for taking simultaneous readings, the furnace may be brought to essentially a constant temperature and the emf of each couple read alternately on one instrument.

When the couples are calibrated by welding or wrapping the junctions together, the difference between the temperatures of the junctions should not be great even when the temperature of the furnace is changing. If it is necessary or advisable to calibrate the couples without removing them from the protection tubes, then the junctions of the couple being tested and that of the standard should be brought as close together as possible in a uniformly heated portion of the furnace. In this case it is necessary that the furnace be brought to approximately a constant temperature before taking observations. It is usually not possible to maintain the reference junctions at 0° C when the couples are completely enclosed in protection tubes. However, extension leads may be used with the couple or the temperature of the reference junctions may be measured with a thermometer.

There are a number of other methods of heating and of bringing the junctions to approximately the same temperature, for example, inserting the couples properly protected into a bath of molten metal or into holes drilled in a large metal block. The block of metal may be heated in a muffle furnace or, if made of a good thermal conductor such as copper, may be heated electrically. Tin, which has a low melting point, 232° C (450° F), and low volatility, makes a satisfactory bath material. The couples should be immersed to the same depth with the junctions close together. Porcelain tubes are sufficient protection, but to avoid breakage by thermal shock when immersed in molten metal it is preferable to place them inside of secondary tubes of iron, nickel-chromium, graphite, or similar material. In all of these methods, particularly in those cases in which the junctions of the couples are not brought into direct contact, it is important that the depth of immersion be sufficient to eliminate cooling or heating of the junctions by heat flow along the thermocouple

and the insulating and protecting tubes. This can be determined by observing the change in the emf of the couple as the depth of immersion is changed slightly. If proper precautions are taken the accuracy yielded by any method of heating or bringing the junctions to the same temperature may be as great as that obtained by any other method.

2. BASE-METAL THERMOCOUPLES IN LABORATORY FURNACES

The methods of testing base-metal thermocouples above room temperature are generally the same as those just described for testing rare-metal couples with the exception, in some cases, of the methods of bringing the junctions of the standard and the couple being tested to the same temperature and the methods of protecting platinum-rhodium standards from contamination. One arrangement of bringing the junction of a platinum-rhodium standard to the same temperature as that of a large base-metal couple for accurate calibration is to insert the junction of the standard into a small hole (about 1.5 mm in diameter) drilled in the hot junction of the base-metal couple as shown in figure 3. The platinum-rhodium standard is protected by porce-

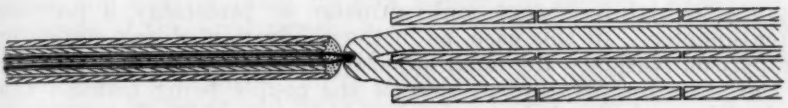

FIGURE 3.—*Arrangement to assure good thermal contact between the junction of a base-metal couple and that of a protected platinum-rhodium couple.*

lain tubes to within a few millimeters of the hot junction, and the end of the porcelain tube is sealed to the couple by pyrex glass or by a small amount of kaolin and water-glass cement. This prevents contamination of the standard couple, with the exception of the small length of 2 or 3 mm, which is necessarily in contact with the base-metal couple. If the furnace is uniformly heated in this region (and it is of little value to make such a test unless it is) contamination at this point will not cause any error. If the wire becomes brittle at the junction this part of the wire may be cut off and enough wire drawn through the seal to form a new junction. The seal should be examined after each test and remade if it does not appear to be good. More than one base-metal couple may be welded together and the hole drilled in the composite junction. The couples should be clamped in place so that the junctions remain in contact. If two potentiometers are used for taking simultaneous readings, the temperature of the furnace may be changing as much as a few degrees per minute during an observation, but if a single instrument is used for measuring the emf, the furnace temperature should be maintained practically constant during observations.

In testing one or more small base-metal couples, they may be welded to the junction of the standard. If a base-metal standard is used, the best method is to weld all the junctions together. If a large number of base-metal couples are to be tested at the same temperature, the method of immersing the couples in a molten-metal bath or into holes drilled in a large copper block is very advantageous. If a tin bath is used, iron or nickel-chromium tubes are sufficient protection for base-

metal couples. When wires, insulators, and protection tubes of base-metal couples are large, tests should be made to insure that the depth of immersion is sufficient to eliminate heating or cooling of the junction by heat flow along these materials.

3. THERMOCOUPLES IN FIXED INSTALLATIONS

After thermocouples have been used for some time at high temperatures, it is difficult if not impossible to determine how much the calibrations are in error by removing them from an installation and testing in a laboratory furnace. The thermocouples are usually inhomogeneous after such use and in such a condition the emf developed by the couples depends upon the temperature distribution along the wires. If possible such couples should be tested under the same conditions and in the same installation in which they are used. Although it is not usually possible to obtain as high a precision by testing the couples in place as is obtained in laboratory tests, the results are far more accurate in the sense of being representative of the behavior of the couples.

The exact method of procedure depends upon the type of installation. A standard couple is usually employed with extension leads and a portable high-resistance millivoltmeter or preferably a portable potentiometer. In this case, as in the calibration of any couple by comparison methods, the main objective is to bring the hot junction to the same temperature as that of the couple being tested. One method is to drill a hole in the furnace at the side of each couple permanently installed, large enough to permit insertion of the checking couples. The hole is kept plugged, except when tests are being made. The standard couple is immersed in the furnace through this hole to the same depth as the couple being tested, with the hot junctions ends of the protection tubes as close together as possible.

In many installations the base-metal couple and protecting tube are mounted inside another protecting tube of iron, fire clay, carborundum, or some other refractory which is permanently cemented or fastened into the furnace wall. Frequently there is room to insert a small test couple in this outer tube alongside of the fixed couple. A third method, much less satisfactory, is to wait until the furnace has reached a constant temperature and make observations with the couple being tested, then remove this couple from the furnace, and insert the standard couple to the same depth.

If desired, comparisons can be made preferably by either of the first or second methods at several temperatures, and a curve obtained for each permanently installed couple showing the necessary corrections to be applied to its readings. Although testing a thermocouple at one temperature yields some information, it is not safe to assume that the changes in the emf of the couple are proportional to the temperature or to the emf. For example, it has been observed that a couple which had changed in use by the equivalent of 9° C at 315° C had changed only the equivalent of 6° C at 1,100° C.

It may be thought that this method of checking couples is unsatisfactory because, in most furnaces used in industrial processes, large temperature gradients exist and there is no certainty that the standard couple is at the same temperature as the couple being tested. This objection, however, is not serious, because if temperature gradients do exist of such a magnitude as to cause much difference in

temperature between two similiarly mounted thermocouples located close together, the reading of the standard couple represents the temperature of the fixed couple as closely as the temperature of the latter represents that of the furnace.

The principal advantage of this method is that the thermocouple, leads, and indicator are tested as a unit and under the conditions of use.

4. THERMOCOUPLES IN STIRRED LIQUID BATHS

Thermocouples and resistance thermometers are not usually directly compared above 300° C because of the difficulty encountered in bringing the thermocouple junction and the thermometer bulb to the same temperature, but these two types of instruments may be very accurately compared below 300° C where a stirred liquid bath can be conveniently used. A type of bath suitable for use above 0° C is shown in figure 5 of a paper by N. S. Osborne.[16] The container, which is insulated on the outside, consists of two cylindrical vertical tubes connected at the bottom and near the top by rectangular ports. A frame carrying the heating element, cooling coils if desired, and stirring propeller are inserted in one of the vertical tubes. The instruments being compared are placed in the other vertical tube and held in place by any convenient means. The chief advantage of this arrangement is that local irregularities due to direct conduction from the vicinity of the heating or cooling elements are eliminated. A stirred liquid bath for use below 0° C has been described by Scott and Brickwedde.[17]

The liquids used in the baths should be capable of being stirred readily at any temperature at which they are used and they should not be highly flammable. At the National Bureau of Standards, oil is used between 100 and 300° C, water in the range 0 to 100° C, mixtures of carbon tetrachloride and chloroform in the range 0 to −75° C, a five-component mixture containing 14.5 percent of chloroform, 25.3 percent of methylene chloride, 33.4 percent of ethyl bromide, 10.4 percent of transdichloroethylene, and 16.4 percent of trichloroethylene in the range −75 to −140° C, and commercial propane below −140° C. Propane is highly flammable, and every precaution must be taken to prevent it from mixing with liquid air or oxygen. A complete series of nonflammable liquids for cryostats is given by C. W. Kanolt [18] for temperatures down to −150° C.

A number of couples can be calibrated at one time in a stirred liquid bath. Platinum-resistance or liquid-in-glass thermometers or thermocouples may be used as standards.

V. METHODS OF INTERPOLATING BETWEEN CALIBRATION POINTS

1. PLATINUM-RHODIUM COUPLES

After a thermocouple has been calibrated at a number of points, the next requirement is a convenient means of obtaining corresponding values of emf and temperature at other points. A curve may be drawn or a table giving corresponding temperature and emf values may be prepared. The values in such a table may be obtained by computing an empirical equation or series of equations through the

[16] Bul. BS 14, 133 (1918–19) S301.
[17] BS J. Research 6, 401 (1931) RP284.
[18] BS Sci. Pap. 20, 619 (1924–26) S520.

calibration points, by direct interpolation between points, or by drawing a difference curve from an arbitrary reference table which closely approximates the temperature-emf relation of the couple. The method to be selected for a particular calibration depends upon such factors as the type of couple, number of calibration points, temperature range, accuracy required, and personal preference.

For the highest accuracy in the range 660 to 1,063° C with platinum to platinum-10 percent rhodium thermocouples, the method is that prescribed in the International Temperature Scale. An equation of the form $e=a+bt+ct^2$, where a, b, and c are constants determined by calibration at the freezing points of gold, silver, and antimony, is used. By calibrating the couple also at the freezing point of zinc and using an equation of the form $e=a'+b't+c't^2+d't^3$, the temperature range can be extended down to 400° C without introducing an uncertainty [19] of more than 0.1° C in the range 660 to 1,063° C. By calibrating the couple at the freezing points of gold, antimony, and zinc and using an equation of the form $e=a''+b''t+c''t^2$, a calibration is obtained for the range 400 to 1,100° C, which agrees (reference 19) with the International Temperature Scale to 0.5° C. The freezing point of copper may be used instead of the gold point, and the aluminum point used instead of the antimony point without introducing an additional uncertainty (reference 19) of more than 0.1° C.

For temperatures outside the range 660 to 1,063° C, the method of drawing a smooth curve through the temperature and emf values has just as much claim to accuracy as the method of passing empirical equations through the calibration points, because an empirical equation performs the same function as a curved ruler. For the temperature range 0 to 1,500° C, a curve for interpolation to 1 or 2° C requires calibration points not more than 200° C apart and a careful plot on a large sheet of paper, which is tedious to read. A reduction in the number of calibration points increases the uncertainty proportionately. If, however, we plot as ordinates the differences between the observed emf and that calculated from the first degree equation $e=10\ t$, and emf as abscissas, the difference at intermediate points may be taken from the curve and added to the quantity $10\ t$ to obtain values of emf corresponding to the appropriate temperature in which the uncertainty in the interpolated values is much less than in the case in which the emf is plotted directly against the temperature. If we go one step further and plot differences from an arbitrary reference table the values of which closely represent the form the temperature-emf relation for the type of couple in question, the maximum differences to be plotted will be only a few degrees. In this way interpolated values are obtained in which the uncertainty in the interpolated values is not appreciably greater than that at the calibration points. The more accurately the values in the arbitrary reference table conform to the emf-temperature relation of actual couples, the fewer the number of calibration points required for a given accuracy.

Reference tables [20] for platinum-rhodium thermocouples which are based on the temperature-emf relations of a considerable number of representative couples from various sources have recently been

[19] Wm. F. Roeser. BS J. Research **3**, 343 (1929) RP99.
[20] Roeser and Wensel. BS J. Research **10**, 275 (1933) RP530.

published. These tables represent accurately the shape of the relations for both the 10 and 13 percent rhodium couples in the entire range 0 to 1,700° C. The difference curve for any couple from the appropriate table is practically a straight line.

In the calibration of platinum to platinum-10 percent rhodium thermocouples to be used as working standards at the National Bureau of Standards, the emf is observed at the freezing points of gold, silver, antimony, zinc, lead, and tin and at the boiling point of water. The constants in the equation $e=a+bt+ct^2$ are computed from the observations at the gold, silver, and antimony points. Values in the range 660 to 1,063° C, computed from this equation and the four observed values below 660° C are used to construct a difference curve from the reference table mentioned previously. This difference curve is then extended graphically above 1,063° C. Values taken from this difference curve when added algebraically to the values in the reference table yield the corresponding temperature-emf values at any temperature. A numerical example follows.

TABLE 4.— *Data for construction of difference curve*

Temperature, t	Observed emf thermocouple H4 e	emf values from table 2, Research Paper 530 e_1	Difference $\Delta e=e_1-e$	Temperature, t	Observed emf thermocouple H4 e	emf values from table 2, Research Paper 530 e_1	Difference $\Delta e=e_1-e$
°C	μV	μV	μV	°C	μV	μV	μV
0.0	0.0	0.0	0.0	700.0	6,269.9	6,260.0	−9.9
100.0	644.0	643.0	−1.0	800.0	7,342.4	7,330.0	−12.4
231.9	1,712.0	1,709.0	−3.0	900.0	8,447.0	8,433.3	−13.7
327.35	2,570.7	2,566.6	−4.1	960.5	9,131.0	9,117.0	−14.0
419.48	3,441.8	3,436.3	−5.5	1,000.0	9,583.9	9,569.0	−14.9
630.5	5,543.5	5,535.0	−8.5	1,063.0	10,316.7	10,301.0	−15.7

The observed values of emf at the calibration points are given in table 4 together with the values at 100° C intervals from 660 to 1,063° C computed from the equation

$$e=-335.4+8.3087\ t+0.0016106\ t^2$$

Corresponding values of e and Δe are plotted in figure 4.

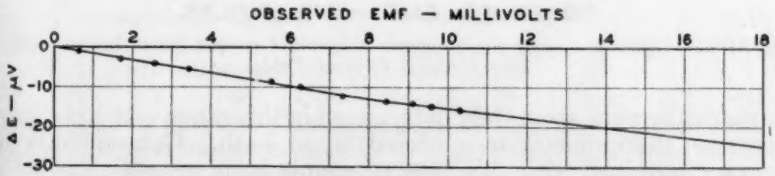

FIGURE 4.— *Difference curve for a platinum 10 percent rhodium couple from reference table in Bureau of Standards Research Paper 530.*

For accurate extrapolation above the gold point it is essential that the shape of the emf-temperature relation given in the reference table conform closely to that of actual thermocouples so that the difference curves will be linear both above and below this point. If the difference curve has a large curvature or if there is an abrupt change in slope above the gold point, the extrapolation of the difference curve

may involve considerable uncertainty. The difference curves of actual thermocouples both 10- and 13-percent rhodium alloys from the reference tables given in Research Paper 530 are in most cases linear in the entire range 0 to 1,700° C and the difference curves can therefore be extrapolated with but little uncertainty. The extrapolated values for a number of thermocouples have been checked by means of actual comparison with an optical pyrometer, and in no case was the difference as great as 3° C at 1,500° C and in most cases it was not over 1° C. These differences are not much greater than the accidental errors in the comparisons.

Difference curves can be drawn from observations obtained in comparison calibrations as well as for observations at fixed points. Two points (accurate to ±1° C at about 600 and 1,200° C) are usually sufficient to determine the difference curve from the tables in Research Paper 530 for either a 10-or a 13-percent rhodium couple, such that the resulting calibration is accurate to ±2° C at any point in the range 0 to 1,200° C and to ±3° C up to 1,500° C.

2. COPPER-CONSTANTAN COUPLES

The relation between the temperature and emf of copper-constantan thermocouples has been very well established in the range −200 to +300° C. The temperature of the measuring junction of such a

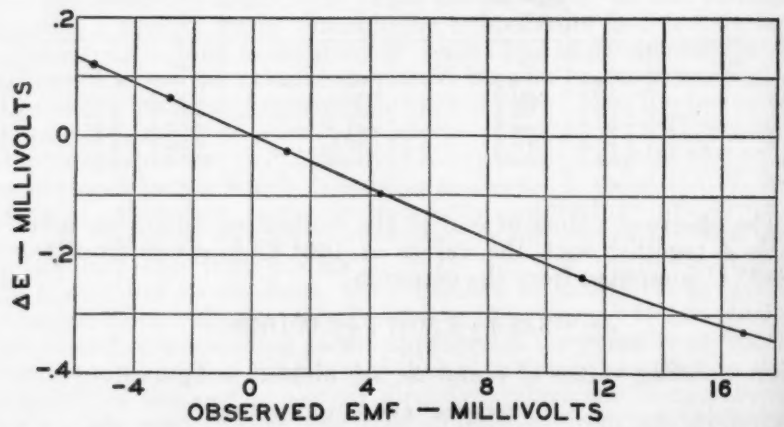

FIGURE 5.—*Difference curve for a copper-constantan couple from Adams' table in International Critical Tables.*

couple can be very accurately determined in this range with a platinum-resistance thermometer in a stirred liquid bath. Consequently the accuracy obtained with this type of couple is, in general, limited by the stability of the constantan wire above 200° C and by the accuracy of the emf measurements or the homogeneity of the wire below 100° C. The stability of the larger sizes of wire is greater than that of the smaller wires under the same conditions.

Figure 5 shows a difference curve from Adams' table[21] for a typical copper-constantan thermocouple. Two points above and two below 0° C suitably spaced are usually sufficient to give an accuracy of 0.3° C.

[21] L. H. Adams. Int. Critical Tables 1, 58 (1926).

Equations are used to good advantage with copper-constantan couples for interpolating between calibration points, but it has not been demonstrated that the accuracy obtained with equations is any greater than that obtained by drawing difference curves from Adams' table except when the differences are large. One convenient method of obtaining a calibration accurate to ±0.2° C in the range 0 to 100° C is to use an equation of the form $e=at+0.04\,t^2$ where a is a constant determined by calibration at 100° C, e the emf in microvolts and t the temperature in ° C. An equation of the form $e=at+bt^2+ct^3$ where a, b, and c are constants determined by calibration at three points (about 100, 200, and 300° C), will give interpolated values as accurately as the couple can be relied upon to retain its calibration (about 0.2° C). The same type of equation with the constants determined at three points about equally spaced in the range 0 to −190° C, may be used in this range to give interpolated values almost as accurately as the emf can ordinarily be measured (about 2μv). An equation of the form $e=at+bt^2$ will yield interpolated values in the range 0 to 100° C almost as accurately as the emf is determined at the calibration points, if the constants are determined by calibration at about 50 and 100° C. The same is true of this equation in the range 0 to −100° C if the constants are determined at −50 and −100° C.

3. CHROMEL-ALUMEL COUPLES

Figure 6 shows a difference curve for a typical chromel-alumel thermocouple from the standard tables published in this issue of the journal (RP767, p. 239). The difference curve from these tables

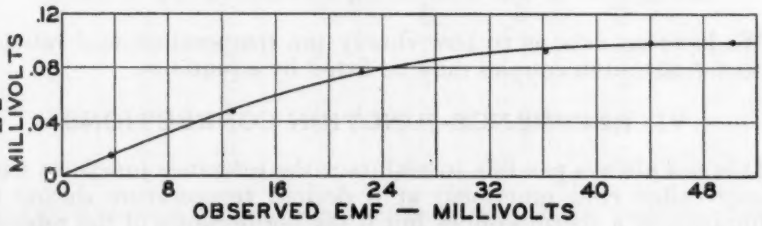

FIGURE 6.—*Difference curve for a chromel-alumel couple from table in Bureau of Standards Research Paper 767.*

can be determined in the range 0 to 1,300° C (2,372° F) with an uncertainty not more than 1° C greater than at the calibration points by calibration at 500, 800, and 1,100° C (or at 1,000, 1,600, and 2,000° F). These tables represent the average temperature-emf relation of chromel-alumel couples now being manufactured.

Little success has been met in fitting equations to the calibration of chromel-alumel thermocouples in the range 0 to 300° C. An equation of the form $e=at+bt^2+ct^3$ will be in error by 1° C at 50° C if the constants are determined by calibration at about 100, 200, and 300° C. However, it will be accurate to about 0.5° C at 150° C and to about 0.2° C between 200 and 300° C. In the range 0 to −190° C, an equation through three points about equally spaced will give interpolated values in which the uncertainty is not more than 2μv greater than at the calibration points.

4. IRON-CONSTANTAN COUPLES

Reference tables have not been determined as accurately for iron-constantan couples as they have for the other types. Skeleton tables are given in Bureau of Standards Technologic Paper T170, page 306, and in the International Critical Tables, volume 1, page 59. Figure 7 shows a difference curve from the table in the International Critical Tables and from a straight line, $e=57t$ (where e is in microvolts and t in °C) for a typical thermocouple. This latter method of drawing difference curves from a straight line is used at the National Bureau of Standards in the calibration of this type of couple.

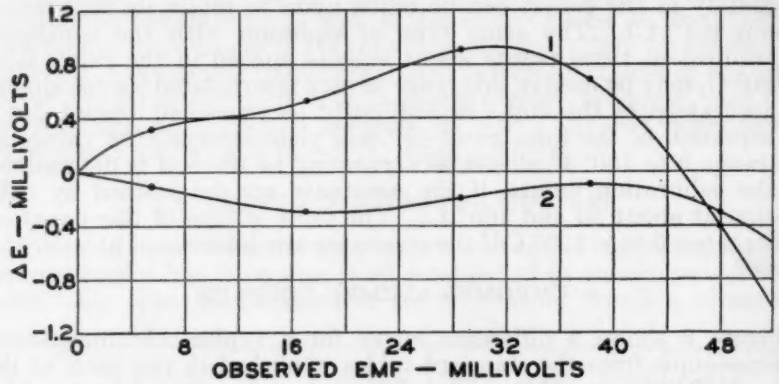

FIGURE 7.—*Difference curves for an iron-constantan couple* (1) *from a straight line; and* (2) *from the table in volume 1 of International Critical Tables.*

We have no data as to how closely the temperature-emf relations of iron-constantan couples may be fitted by equations.

VI. REFERENCE-JUNCTION CORRECTIONS

It is not always possible to maintain the reference junctions (commonly called cold junctions) at a desired temperature during the calibration of a thermocouple, but if the temperature of the reference junctions is measured it is possible to apply corrections to the observed emf which will yield a calibration with the desired reference-junction temperature. If the emf of the couple is measured with the reference junctions at temperature t, and a calibration is desired with these junctions at temperature t_o, the measured emf may be corrected for a reference-junction temperature of t_o by adding to the observed value the emf which the couple would give if the reference junctions were at t_o and the measuring junction at t. For example, suppose the observed emf of a platinum-10 percent rhodium thermocouple with the measuring junction at 1,000° C and the reference junction at 25° C is 9.43 mv, and the emf of the couple with the measuring junction at 1,000° C and the reference junctions at 0° C is required. The emf of the couple when the reference junctions are at 0° C and the measuring junction at 25° C is 0.14 mv, then the sum of these emf (9.43 and 0.14) gives the desired value.

The sign of the corrections must be considered when applying these corrections, for example, suppose the observed emf of the couple with the measuring junction at 1,000° C and the reference

junctions at 0° C is 9.57 mv and the emf of the couple with the measuring junction at 1,000° C and the cold junctions at 25° C is required. The emf of the couple when the reference junction is at 25° C and the measuring junction at 0° C is −0.14 mv, and when this is added to the observed emf the desired value 9.43 mv is obtained. Whether the reference-junction correction is positive or negative should not cause any confusion if it is remembered that the emf of the couple is lowered by bringing the junction temperatures closer together and increased by making the difference greater.

In the calibration of couples the temperature-emf relation is not always accurately determined in the range of reference-junction temperatures, in which case the average temperature-emf relation of the type of couple may be used. The average relations for the various types of couples are given in table 5. The errors caused by using these average relations instead of the actual relation for a particular couple are, in general, less than 1° C.

TABLE 5.—*Average temperature-*emf *relations for thermocouples for applying reference-junction corrections*

Temperature		Electromotive force			
		Platinum-rhodium [1]	Chromel-alumel	Iron-constantan	Copper-constantan
°C	°F	mv	mv	mv	mv
−20	−4	−0.101	−0.77	−1.02	−0.75
−15	5	−.077	−.58	−.77	−.57
−10	14	−.052	−.39	−.51	−.38
−5	23	−.026	−.20	−.26	−.19
0	32	.000	.00	.00	.00
5	41	.027	.20	.26	.19
10	50	.054	.40	.52	.39
15	59	.082	.60	.78	.59
20	68	.111	.80	1.05	.79
25	77	.141	1.00	1.31	.99
30	86	.171	1.20	1.58	1.19
35	95	.201	1.40	1.84	1.40
40	104	.232	1.61	2.11	1.61
45	113	.264	1.81	2.37	1.82
50	122	.297	2.02	2.64	2.03

[1] The values in this column apply for either the 10- or 13-percent rhodium couple. The difference between the average temperature-emf relations in this range does not exceed 5 μv.

If the thermocouple is very short, so that the reference junctions are near the furnace and subject to considerable variations or uncertainty in temperature, it is usually more convenient to use extension leads to transfer the reference junctions to a region of more constant temperature than to measure the temperature of the reference junctions near the furnace. The extension leads of base-metal couples are usually made of the same materials as the thermocouple wires, but in the case of platinum-rhodium couples a copper lead is connected to the platinum-rhodium wire and a copper-nickel lead to the platinum wire. Leads for any of the couples discussed here are available at all the pyrometer instrument manufacturers. Although the temperature-emf relation of the copper, copper-nickel lead wire is practically the same as that of platinum-rhodium couples, the individual lead wires are not identical thermoelectrically with the couple wires to which they are attached and, therefore, the two junctions where the

leads are attached to the couple should be kept at nearly the same temperature. This is not necessary in the case of base-metal couples when each lead and couple wire to which it is attached are the same material.

VII. TESTING OF THERMOCOUPLE MATERIALS

Thermocouples are ordinarily made up to yield a specified emf at one or more temperatures, and in order to select and match materials to do this a convenient method of testing each element is required. One method of accomplishing this is to determine the thermal emf of the various materials against some stable and reproducible material. At low temperatures copper is sometimes used for this purpose, but platinum appears to be the most satisfactory because it can be used at any temperature up to its melting point, can be freed from all traces of impurities, and can be readily annealed in air. Two samples of platinum, both of which are spectrochemically pure, may differ slightly in thermal emf, but the same is true of any other metal. To avoid the ambiguity that might arise from this fact, the thermal emf of thermocouple materials tested at the National Bureau of Standards (since 1922) is referred to an arbitrary piece of platinum designated as standard Pt 27. This standard is spectrochemically pure, has been thoroughly annealed, and although it may not be the purest platinum that has been prepared, serves as a satisfactory standard to which the thermal emf of other materials may be referred. However, there is nothing to prevent any other laboratory from setting up a laboratory standard for their own use, but in order that the various laboratories and manufacturers may specify and express values of thermal emf on a common basis, a common and ultimate standard is necessary.

Platinum is used as a working standard for testing thermocouple materials in some laboratories, but it is generally more convenient to use a working standard of the same material as that being tested. In any case the thermal emf of a material against the standard Pt 27 is the algebraic sum of the emf of the material against the working standard and the emf of the working standard against the standard Pt 27 (the law of intermediate metals). When platinum is used as a working standard in testing some other material, the thermal emf measured is large. To obtain the thermal emf of the material against the standard Pt 27, the relatively small emf of the platinum working standard against the standard Pt 27 is added to the large measured emf. When the working standard is of the same kind of material as that being tested, the thermal emf measured is small. To obtain the thermal emf of the material against the standard Pt 27 in this case, the relatively large emf of the working standard against the standard Pt 27 is added to the small measured emf.

Except in the case of constantan, two samples of a similar material which will develop more than 0.5 μv/°C against one another are exceptional. In most cases the value is less than 0.2 μv/°C. Even in the case of constantan, the thermal emf between 2 extreme samples does not exceed 3 μv/°C. Therefore, in determining the difference in thermal emf between two samples of a similar material, it is not necessary to measure the temperature accurately.

The average thermal emf/°C of platinum against other thermocouple materials is given in table 6. It is seen that in measuring the thermal emf of these materials directly against platinum working standards, it is necessary to measure an emf which changes by a large amount for a small change in temperature. An accurate measurement of the emf corresponding to a given temperature, therefore, requires an accurate measurement of the temperature of the junctions. The necessity for this accurate measurement of temperature, however, is avoided when the measurements are made by using a working standard of material similar to that being tested, since in this case the emf developed is small and changes very little even for large changes in temperature. In the latter method, the accurate measurement of temperature is not entirely avoided but merely shifted to the laboratory that determines the thermal emf of the working standards against the standard Pt 27.

TABLE 6.—*Average thermal* [1] emf/°C *of platinum against other thermocouple materials*

Material	Temperature	Average change in thermal emf with temperature
	°C	μv/°C
Platinum-10 percent rhodium	1,000	11.5
Platinum-13 percent rhodium	1,000	13.0
Chromel	870	31.7
Alumel	870	8.7
Iron	600	11.4
Constantan	600	47.0
Constantan	100	37.0
Copper	100	9.25

[1] Complete tables giving the average thermal emf of platinum-10 percent rhodium, and platinum-13 percent rhodium against platinum are given in Research Paper 530. The average thermal emf of chromel and of alumel against platinum are given in Research Paper 767.

The small thermal emf of a platinum working standard against the standard Pt 27 at any temperature can be determined as accurately as the emf can be measured. These standards are subject to change during use but, if properly used and occasionally checked, can be relied upon to about 10 μv at 1,000° C. The thermal emf of working standards of other materials is determined and certified at the National Bureau of Standards to the equivalent of ±2° C at high temperatures.

In any event the testing of a thermocouple material is essentially the determination of the emf of a thermocouple in which the material being tested is one element and a working standard the other. Some of the precautions that must be observed to obtain accurate results are given in the following sections.

1. PLATINUM

The thermal emf of thermocouple platinum against the standard Pt 27 is usually less than 100 μv at 1,200° C and in testing one sample of platinum against another it is not necessary to measure the temperature of the hot junction to closer than 25° C to obtain a comparison accurate to 2 μv. The reference-junction temperature need not be accurately controlled. The platinum standard (i. e., the wire

previously compared with the standard Pt 27) is welded to the wire being tested to form a couple and the emf measured at one or more temperatures by any of the methods described for calibrating platinum-rhodium thermocouples. The wires should be carefully insulated and protected. Measurements at two temperatures, about 600 and 1,200° C, are sufficient to give the emf at any temperature as the emf is small and practically proportional to the temperature.

In many laboratories the platinum standard and the platinum element of the couple used to measure the temperature are one and the same. The sample or wire being tested is then welded to the junction of the couple and the emf of the couple and that between the two platinum wires are measured simultaneously with two potentiometers or alternately with one instrument. Simultaneous readings of these electromotive forces should not be made with a millivoltmeter or with a current flowing in either circuit because one wire is common to both circuits and in this case the potential difference measured by one instrument is influenced by the current flowing in the other circuit. However, this objection is not encountered in the method described above in which the platinum standard is not the same wire as the platinum of the thermocouple.

2. PLATINUM-RHODIUM

The testing of platinum-rhodium thermocouple wire directly against platinum is exactly the same as the calibration of platinum-rhodium thermocouples. Platinum against platinum-10 percent rhodium gives 11.5 μv/°C and platinum against platinum-13 percent rhodium gives about 13 μv/°C at 1,000° C. Therefore, in order to determine the thermal emf of a sample of platinum-rhodium against platinum to ± 20 μv, it is necessary to measure the temperature to ± 1.5° C. Such an accuracy in temperature measurements is obtained only with a very homogeneous and accurately calibrated couple in a uniformly heated furnace, but if the emf of one sample of wire is known with this accuracy, it may be used to determine the emf of other samples without the necessity of accurately measuring the temperature. For example, the thermal emf per degree of any sample of platinum-10 percent rhodium against any other sample rarely exceeds 0.2 μv/°C (200 μv at 1,000° C). Therefore, if the thermal emf of one sample against platinum is known to ± 20 μv at 1,000° C, the emf of other samples against the same platinum can be determined to about the same accuracy by comparing the samples of platinum-rhodium and measuring the temperature of the hot junction to 10 or 20° C. The same applies for platinum-13 percent rhodium.

The working standard used to determine the thermal emf of the platinum-rhodium may be a sample of platinum, of platinum-rhodium, or either element of the thermocouple used in measuring the temperature. Platinum-10 percent rhodium against platinum-13 percent rhodium gives about 1.5 μv/°C at 1,000° C so that if the thermal emf of one of these materials against platinum is known to ± 20 μv at 1,000° C, the thermal emf of the other against the same platinum can be determined to ± 30 μv by comparing the two and measuring the temperature to ± 6° C.

A number of wires can be welded together and tested by any of these methods.

3. BASE-METAL THERMOCOUPLE MATERIALS

(a) AT HIGH TEMPERATURES

In testing base-metal thermocouple materials (alumel, chromel, constantan, copper, and iron) the procedure is very much the same as in calibrating base-metal thermocouples. Although such thermal-emf measurements are ultimately referred to platinum, it is not necessary to measure each sample directly against platinum. When the measurements are made against platinum (and this must frequently be done), the platinum wire should be sealed through the end of a glazed porcelain protection tube with pyrex glass, leaving about 1 cm of the wire exposed for welding to the base-metal wire or wires. The largest uncertainty in the measurements arises from the uncertainty in the determination of the temperature of the junction. The junction of a standard platinum-rhodium couple may be inserted into a hole drilled in the junction formed by welding the material to platinum. This brings the junctions to the same temperature.

In the use of platinum or platinum-rhodium for testing thermocouple materials, the wires are used a large number of times before checking or scrapping. Base-metal thermocouple wires used for testing similar materials should not be used more than once if the highest accuracy is required, because there is a slight change in these materials when heated to a high temperature and if they are used repeatedly, the wires become inhomogeneous. The procedure then is to select a coil of wire and test it for homogeneity by taking several samples from different parts of the coil, welding them all together, and measuring the emf between the various samples. If the coil is sufficiently homogeneous as found from such tests, one or more samples may be taken from it and the thermal emf determined as accurately as necessary by comparison with a standard, the emf of which against the standard Pt 27 is known. The average value for the thermal emf of the few selected samples from the coil against the standard Pt 27 will apply for the remainder of the coil with sufficient accuracy for most purposes. Any sample from this coil may then be used as a working standard [22] for testing similar materials. The accuracy with which the temperature must be measured depends upon the difference between the standard and the material being tested. In case of some materials that have been well standardized, the differences are small enough that an accuracy of 50° C is sufficient. Seldom, if ever, should it be necessary to measure the temperature closer than 10° C.

(b) AT LOW TEMPERATURES

Annealed electrolytic copper is very uniform in its thermoelectric properties and is often used as a standard for thermoelectric testing at temperatures below 300° C. The thermal emf of other materials against either copper or platinum may be determined very accurately by using a stirred liquid bath or fixed points. The steam point is an excellent one for this purpose.

Table 7 gives the thermal emf of annealed electrolytic copper against National Bureau of Standards standard Pt 27 and may be used to convert values of the thermal emf of any material against one of these

[22] Working standards of chromel and alumel prepared in this way, with certificates giving the thermal emf of the individual samples against the standard Pt 27 may be procured from the National Bureau of Standards.

standard materials to values of emf of the same material against the other standard material.

TABLE 7.—*Thermal* emf *of annealed electrolytic copper against* NBS *platinum standard* Pt 27

Temperature	Electromotive force	Temperature	Electromotive force
°C	μv	°C	μv
−200	−194	100	766
−150	−354	150	1,265
−100	−367	200	1,831
−50	−242	250	2,459
0	0	300	3,145
+50	+340	350	3,885

4. REFERENCE-JUNCTION CORRECTIONS

It is not convenient for everyone to obtain the same reference-junction temperature in determining the emf of the various thermocouple materials against platinum and, therefore, corrections must be applied to arrive at values for a common reference-junction temperature. The method of applying these corrections is the same as that discussed under the testing of thermocouples. The average temperature-emf relations for the various thermocouple materials against platinum are given in table 8 and may be used for making reference-junction corrections.

TABLE 8.—*Average temperature-*emf *relations of various thermocouple materials against platinum for applying reference-junction corrections*

Temperature		Electromotive force					
		Platinum-rhodium [1] *vs.* platinum	Alumel-platinum	Chromel-platinum	Constantan-platinum	Copper-platinum	Iron-platinum
°C	°F	mv	mv	mv	mv	mv	mv
−20	−4	−0.101	−0.27	−0.50	−0.64	−0.109	−0.38
−15	5	−0.077	−0.20	−0.38	−0.48	−0.084	−0.29
−10	14	−0.052	−0.14	−0.25	−0.32	−0.057	−0.19
−5	23	−0.026	−0.07	−0.13	−0.16	−0.029	−0.10
0	32	0.000	0.00	0.00	0.00	0.000	0.00
5	41	0.027	0.07	0.13	0.16	0.030	0.10
10	50	0.054	0.14	0.26	0.33	0.060	0.19
15	59	0.082	0.20	0.40	0.50	0.091	0.28
20	68	0.111	0.27	0.53	0.67	0.124	0.38
25	77	0.141	0.34	0.66	0.84	0.158	0.47
30	86	0.171	0.41	0.79	1.01	0.193	0.57
35	95	0.201	0.47	0.93	1.18	0.229	0.66
40	104	0.232	0.54	1.07	1.35	0.265	0.76
45	113	0.264	0.60	1.21	1.52	0.302	0.85
50	122	0.297	0.67	1.35	1.69	0.340	0.95

[1] These values apply for either 10- or 13-percent rhodium.

In comparing two samples of a similar thermocouple material at high temperatures, it is not necessary to measure or control accurately the temperature of the reference junctions. The emf developed by two samples of platinum-rhodium, even the 10 against the 13-percent rhodium alloy, is practically independent of the temperature of the reference junctions between −20 and +50° C. In all other cases,

with the possible exception of iron, the emf may be taken as proportional to the difference between the temperatures of the two junctions, and when the emf is small, the corrections for the temperature changes of the reference junctions are negligible. In comparing two samples of iron, the emf developed is changed more by changing the temperature of the reference junctions than by changing that of the hot junction by the same amount, for example it was observed (in one case) that the emf (320 μv) developed by two samples of iron when one junction was at 600° C and the other at 25° C changed by 0.1 μv for each degree change in the temperature of the hot junction and 1.4 μv for each degree change in the temperature of the reference junctions.

VIII. ACCURACIES OBTAINABLE

The accuracies obtained in calibrating the various types of thermocouples by different methods and the uncertainty in the interpolated values by various methods are given in table 9.

TABLE 9.—*Summary of methods and accuracies obtainable in calibrating thermocouples*

Type of thermocouple	Methods of calibration	Temperature range	Calibration points	Accuracy at observed points	Method of interpolating	Uncertainty in interpolated values
		°C		°C		°C
Platinum-10 percent rhodium	International Temperature Scale, fixed points.	660 to 1,063	Freezing point of Sb, Ag, and Au.	0.2	*Equation:* $e=a+bt+ct^2$	0.2
Platinum-rhodium [1]	Fixed points	0 to 1,500	Boiling point of water, freezing point of Sn, Pb, Zn, Sb, Ag, and Au.	0.2	Difference curve from reference table.	0.5 to 1,100 and 2 at 1,500
	NBS standard samples, fixed points.	0 to 1,500	Freezing point of Sn, Zn, Al, and Cu.	0.2	do	1 to 1,100 and 2 at 1,500
	Comparison with standard couple.[1]	0 to 1,500	About every 100° C	1	Any	2 to 1,100 and 3 at 1,500
	do	0 to 1,500	About 600 and 1,200° C (or more points).	1	Difference curve from reference table.	2 at 1,100 and 3 at 1,500
Chromel-alumel	Comparison with standard couple.[1]	0 to 1,200	About every 100° C	2	Any	3
	do	0 to 1,200	About 500, 800, and 1,100° C (or more points).	2	Difference curve from reference table.	3
	Comparison with standard resistance thermometer [2] or at fixed points.	0 to 350	About every 100° C	0.1	do	0.5
	Comparison with standard resistance thermometer.[2]	0 to −190	About every 60° C	0.1	do	0.5
Iron-constantan	Comparison with standard couple.[1]	0 to 750	About every 100° C	2	Any	3
	do	0 to 750	About 100, 300, 500, and 750° C	2	Difference curve from straight line.	4
	Comparison with standard resistance thermometer [2] or at fixed points.	0 to 350	About every 100° C	0.1	do	1
	Comparison with standard resistance thermometer.[2]	0 to −190	About every 60° C	0.1	do	1
	Comparison with a standard resistance thermometer [2] or	0 to 300	About every 100° C	0.1	*Equation:* $e=at+bt^2+ct^3$ or	0.2

Copper-constantan	Comparison with a standard resistance thermometer [2] or at fixed points.	0 to 300	About every 100° C	0.1	*Equation:* $e=at+bt^2+ct^3$ or difference curve from reference table.	0.2
	Comparison with a standard resistance thermometer.[2]	0 to 100	About 50 and 100° C	0.05	*Equation:* $e=at+bt^2$ or difference curve for reference table.	0.1
	Fixed point	0 to 100	Boiling point of water	0.05	*Equation:* $e=at+0.04\,t^2$	0.2
	Comparison with a standard resistance thermometer.[2]	0 to −190	About every 60° C	0.1	*Equation:* $e=at+bt^2+ct^3$ or difference curve from reference table.	0.2
	Fixed points	0 to −190	Sublimation point of CO_2 and boiling point of O_2.	0.1	Difference curve from reference table.	0.3

[1] Either 10- or 13-percent rhodium.

[2] In a stirred liquid bath.

These accuracies may be obtained with homogeneous thermocouples when reasonable care is exercised in the work. More or less accurate results can be obtained by the same methods. In the case of chromel-alumel and iron-constantan couples at low temperatures, the accuracy given in table 9 is limited by the uncertainty in interpolated values. However, this uncertainty can be greatly reduced by observing the emf of the couples at more points. The accuracy obtained with copper-constantan couples at low temperatures is usually limited by the emf measurements and in such cases the accuracy may be improved by employing a number of couples in series (multiple-junction couples).

When it is desired to test a thermocouple and leads or thermocouple, leads, and indicator as a unit by any of the methods described in the preceding sections, no additional difficulties are encountered.

Table 10 gives the uncertainty in the thermal emf measurements of various thermocouple materials against the standard Pt 27 produced either by an uncertainty of ±2° C in the temperature measurements

TABLE 10.—*Uncertainty in the determination of the thermal* emf *of thermocouple materials against platinum*

Material	Uncertainty in electromotive force
	mv
Platinum	
Platinum-10 percent rhodium	0.03
Platinum-13 percent rhodium	.03
Alumel	.02
Chromel	.07
Constantan	.10
Iron	.03

when platinum is used as a working standard, or by an uncertainty of ±10° C in the temperature measurements when the material is compared with a working standard of the same material, the emf of which has been previously determined against the standard Pt 27 to the equivalent of ±2° C. In the former case the uncertainty in the emf measurement is proportional to the uncertainty in the temperature measurement, whereas in the latter case it depends only slightly upon the temperature measurement provided the emf of the working standard against the standard Pt 27 is known to the same accuracy.

The following services are provided by the National Bureau of Standards for fees covering the cost.

(1) Thermocouples are calibrated and certified as accurately as the conditions of use and the homogeneity and stability of the wires justify. The accuracies given in table 9 have been found to meet most needs.

(2) Indicators used with thermocouples are calibrated separately or in combination with a particular thermocouple.

(3) The thermal electromotive forces of thermocouple materials against the standard Pt 27 are determined and the results certified to the limits justified by the material.

(4) Standard samples of thermocouple materials are distributed with certificates giving the thermal electromotive forces of the individual samples against the standard Pt 27. The materials being distributed at present are alumel and chromel P.

(5) Standard samples of metals are distributed, each with a certificate giving the value of the freezing point. The freezing-point metals being distributed at present are tin, lead, zinc, aluminum, and copper.

WASHINGTON, December 31, 1934.

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MULTIFREQUENCY IONOSPHERE RECORDING AND ITS SIGNIFICANCE[1]

By Theodore R. Gilliland

ABSTRACT

Results obtained in hourly measurements of critical frequencies of the layers of the ionosphere are presented for the period of a year between May 1933 and April 1934. The critical frequencies were obtained by an automatic recorder which covers the frequency band 2,500 to 4,400 kc/s at a uniform rate of 200 kc/s per minute. Critical frequencies in this band are for the E and F_1 layers in the daytime and for the F layer at night. Graphs are presented which represent hourly averages of critical frequencies for each layer for each month. The points from which the averages are obtained are also plotted to show the scatter. The critical frequencies for the E and F_1 layers follow in phase with the sun both diurnally and seasonally. During the day "fine structure" is often in evidence, indicating other strata between the usual E and F_1 layers. The results obtained for the F layer during the winter night are of particular interest. After dropping to a minimum near midnight the critical frequency increases to a maximum at about 4 a.m., then drops to a second minimum before sunrise. This increase during the night represents more than a 100 percent increase of maximum electron density.

The results for the period September 11 to 30, 1933, are compared with those for the same period of 1934, showing a considerably greater ionization density for the latter period. The minimum point of the average curve for 1934 is about 180 kc/s higher than that for 1933. Whether or not this increase is connected with the new sun-spot cycle is not yet certain.

Some of the results have been studied in connection with a practical communication problem, which was concerned with skipping of signals in short-distance transmission along one of the airways. The results are used to determine the limiting frequency for any distance up to a few hundred miles.

Information of the type presented here should prove useful in the study of the properties of the upper atmosphere, as well as in the interpretation of communication problems.

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I. INTRODUCTION

The purpose of this paper is to present some of the results obtained with an automatic recorder which gives the relation between the radio frequency of the pulse signals used and the virtual height reached by them in that portion of the upper atmosphere now called the ionosphere. With records of this type it is possible to interpret some of the characteristics of radio waves which travel by way of the ionosphere.

[1] Presented in part at Washington meeting of URSI, Apr. 27, 1934.

The equipment, which has been described previously,[2] employs the pulse method of Breit and Tuve with modifications which permit automatic recording. The system consists of a transmitter, receiving set, and galvanometer oscillograph with photographic attachment. The transmitter is made to send out short pulses, which arrive at the receiving set via the ionosphere as well as directly from the transmitter. By passing the output of the receiving set through the oscillograph a photographic record is made which gives a measure of the virtual height reached by the pulses. The frequency of the transmitting and receiving sets which are placed in the same room is shifted continuously from 2,500 to 4,400 kc/s at the uniform rate of 200 kilocycles per second per minute, thus requiring 9½ minutes for each record. During most of the time records are made once each hour although at times they are made each half hour. This work is being carried on at the National Bureau of Standards field station near Beltsville, Md., (lat. 39°2′ N.; long. 76°51.5′ W.).

During the daytime the band of frequencies used (2,500 to 4,400 kc/s) indicates the presence of at least three strata. For the lower range of frequencies the waves are returned from the E layer with a virtual height of about 110 to 120 km. As the frequency is increased the waves pass through the E layer and are returned from the F_1 layer with a virtual height usually between 180 and 240 km. As the frequency is increased still further the waves penetrate the F_1 layer and are returned from the F_2 layer with a virtual height of 280 km or more. In the late afternoon the F_1 and F_2 layers appear to merge so that at night only one well-defined layer is in evidence in the F region with a virtual height of 240 km and higher. As the ion density decreases in the evening, frequencies above 2,500 kc/s are no longer returned from the E layer. Later at night the highest frequencies in this band finally penetrate the F layer and are no longer returned at normal incidence (i. e., for transmission straight up and straight down). Occasionally the ion density becomes so low that even 2,500 kc/s is not returned. The lowest frequency which just passes through a layer at normal incidence is called the critical frequency of the layer. The discussion that follows deals mainly with the measurements of the critical frequencies of the E and the F_1 layers in the daytime and of the F layer at night. Besides the more or less regular refraction phenomena discussed above there are sporadic reflections from the E region which appear at almost any time but most often during the summer. Also reflections from the F region for frequencies above the usual critical values appear at times. That this sporadic phenomenon is reflection rather than refraction is indicated by the character of the pattern obtained. The usual F-layer refraction with critical frequencies for both ordinary and extraordinary rays is often "visible" through an E layer which can support several multiple reflections. The character of these sporadic reflections is shown in some of the records that follow.

The data discussed here were obtained over a period of a year between May 1933 and April 1934, inclusive. Also some of the data obtained during September 1934, are compared with those of September 1933.

[2] Theodore R. Gilliland. BS J. Research **11**, 561 (1933) RP608; also Proc. Inst. Radio Engrs. **22**, 236 (1934).

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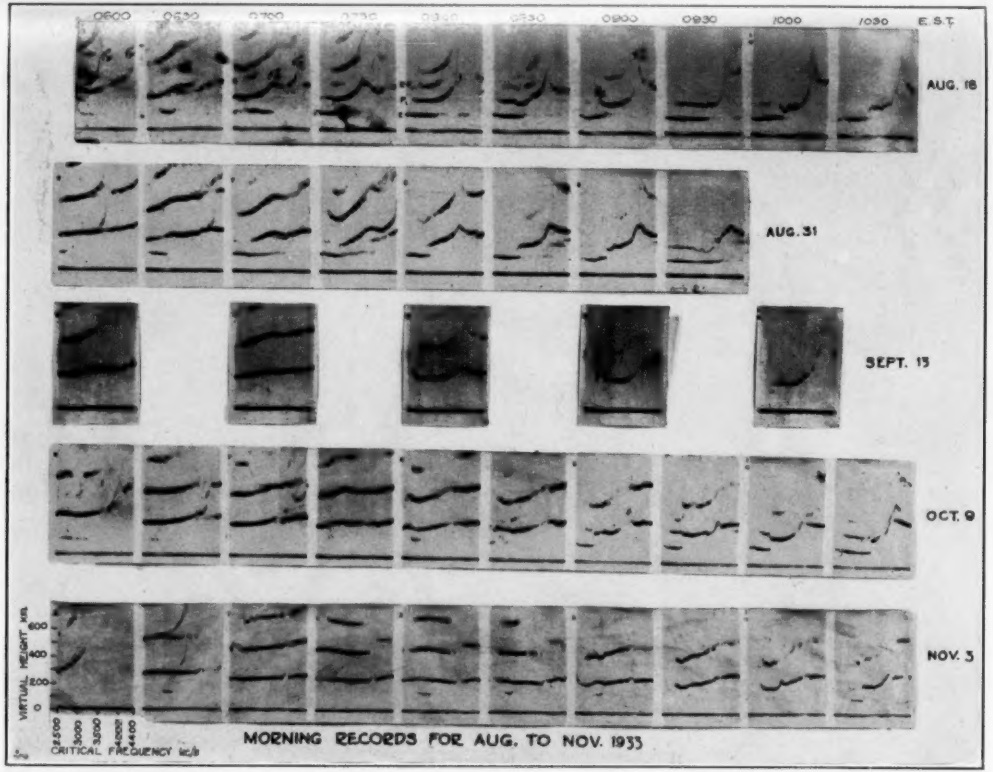

FIGURE 1.—*Records taken during the morning at half-hour intervals showing the changes in character of the patterns from August to November 1933.*

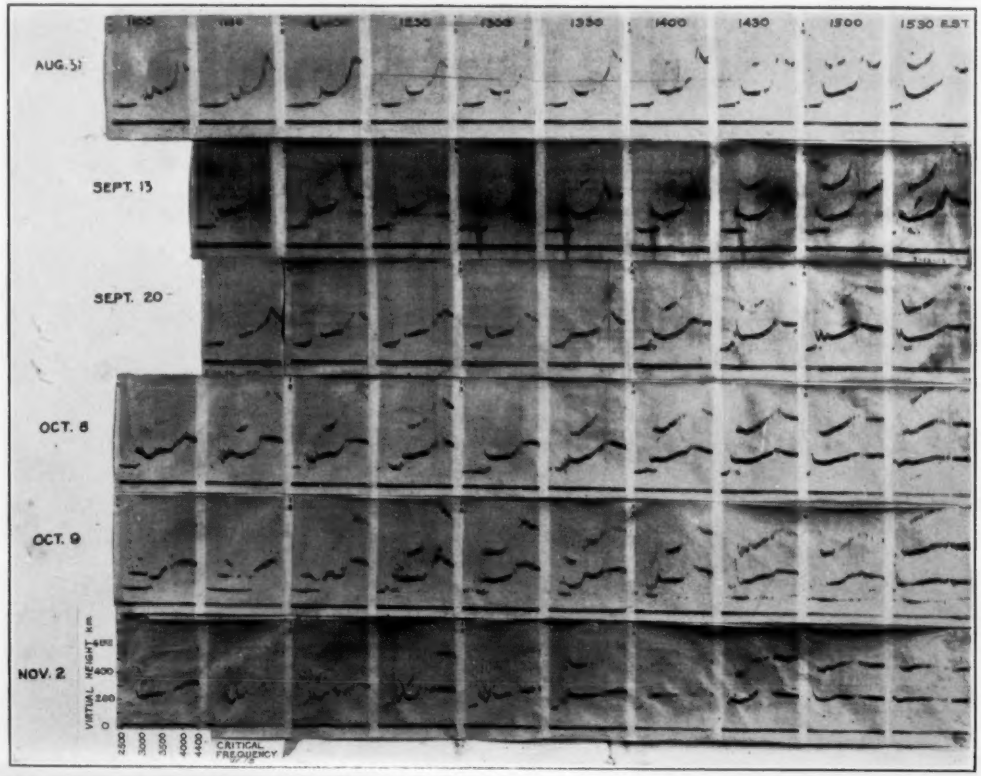

FIGURE 2.—*Records showing changes in the character of the patterns from August to November 1933 between 1100 and 1530, eastern standard time.*

II. DAYTIME E AND F_1 LAYER RESULTS

The type of record obtained during the daytime is shown in figures 1 and 2. In figure 1 records taken during the morning at half-hour intervals show the changes with season from August to November 1933. Each small section of record gives the virtual height for the band from 2,500 to 4,400 kc/s. The interpretation of patterns of this type has been given previously [3 4] and will not be discussed in detail here. The record at 0600 EST for August 18 shows the ordinary and extraordinary rays returned from the F region with the critical frequencies f''_F and f'_F.[5] The critical frequency for each ray occurs at the point where the trace approaches the vertical. By 0700 the ordinary ray critical frequency is above 4,000 kc/s and formation of the F_1 layer is beginning to appear. The pattern at 0800 shows F_1 refraction with one multiple, as well as both E and E-F [6] reflections. E-F reflections are those which penetrate the E layer, then make two round trips between the top of the E and the bottom of the F layers before finally coming down through the E layer to earth. This type of reflection is quite common and can be differentiated from the others because its trace has the same shape as that of the F-layer trace below it, while its separation from the F trace is about the same as the separation between the E and F traces. This indicates that the reflecting E layer is fairly thin at times, perhaps less than 10 km in thickness when E-F reflections appear.

The pattern at 0900 shows both the E and F_1 critical frequencies. The F_1 critical frequency becomes more pronounced later in the morning. This critical frequency is for the ordinary ray. The extraordinary ray can be seen at times, but its critical frequency is usually above the limits of the present recording system.

The F-layer stratification is seen to become less pronounced and the decrease in both the E and F_1 critical frequencies can be seen as winter approaches. The records of figures 2 show the changes from August to November 1933, between 1100 and 1530. At 1100 on August 31 there is a triple critical effect between the usual E and F_1 layers. "Fine structure" of this type which has been noted by other observers is quite common and indicates other strata between the usual layers. Multiple critical frequencies occur at times of rapid increase in ionization, especially at sunrise. This is to be expected because the rate of change of frequency is not great enough to keep up with the rapid increase in ionization. It is not likely, however, that this is the cause of the fine structure shown above. At 1130 there are only two critical frequencies between E and F_1, and at 1200 and after there is only one. Fine structure is in evidence on many of the other records of figure 2. It should be pointed out that many of the patterns recorded are very complex and that it is often

[3] Theodore R. Gilliland. BS J. Research 11, 561 (1933) RP608; also Proc. Inst. Radio Engrs. **22**, 236 (1934).

[4] For a discussion of the theory see Kirby, Berkner, and Stuart, BS J. Research **12**, 15 (1934) RP632; also Proc. Inst. Radio Engrs. **22** (February 1934).

[5] The following nomenclature for critical frequencies is used:
f_E for E-layer critical frequency.
f''_{F_1} for F_1-layer critical frequency. Ordinary ray.
f'_{F_1} for F_1-layer critical frequency. Extraordinary ray.
f''_F for F-layer critical frequency. Ordinary ray.
f'_F for F-layer critical frequency. Extraordinary ray.
Attention has just been called to nomenclature adopted at the London meeting of the URSI in September 1934. The URSI nomenclature will be used in future publications.

[6] Called M reflections by Ratcliffe and White in England.

difficult and sometimes impossible to interpret the results. With three or more layers, some of them giving double refraction, and with reflections directly from, as well as back and forth between layers, added to multiple reflections and refractions, it can be understood that some of the patterns will be quite complex.

The results of the year's measurements of E-layer critical frequencies are shown in the graphs of figures 3, 4, and 5. The time scale is divided into half-hour intervals and the frequency scale is divided into intervals of 50 kc/s. The points falling within a given interval are plotted within the rectangle corresponding to that interval. When there is only one critical frequency it is shown as a dot. When the critical frequencies are multiple (i. e., when fine structure exists) as shown in figure 2, the lowest one is plotted as a dot and the second one as a cross. The values higher than the second are not indicated.

The curves represent hourly averages of the lowest critical frequencies. The points representing measurements on the half hour are not included in the average curves because they are relatively few in number compared to the hourly measurements. The averages for the second critical frequency are not shown. The curves for May, June, and July are dotted because the measurements were relatively few in number during these months and the average value shown may not represent an accurate average for the month. It is likely that the maximum of the average curves for May and June should be higher. Most of the curves show some irregularity, which can be understood, considering the wide scatter of the points. Some of the scatter may be caused by the fact that one of the critical frequencies of a multiple group may disappear between records and it is usually impossible to tell which one is missing. As a result, the lowest one of the group which appears in the average curve may actually represent the critical frequency for a higher stratum. The maximum of the average critical-frequency curve for each month is shown in table 1. In each case the maximum comes very near to noon.

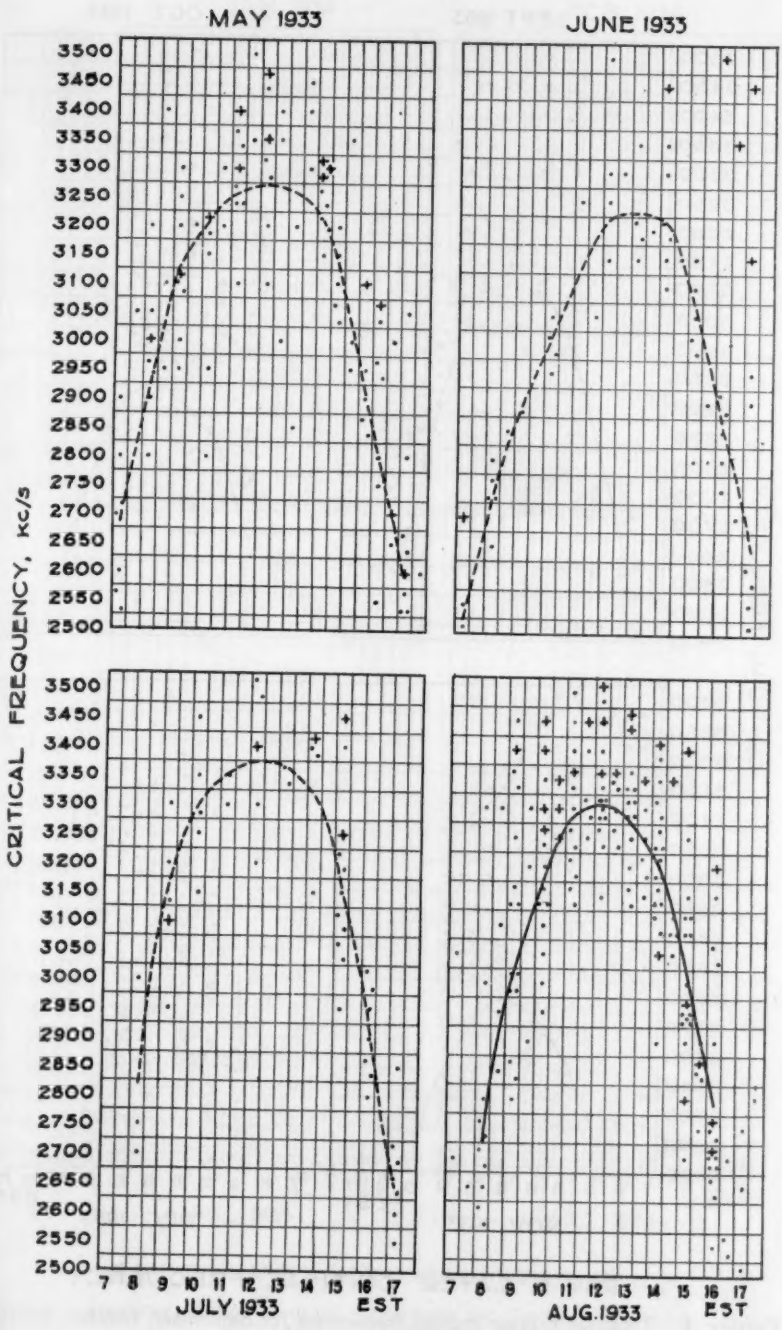

FIGURE 3.—*Daytime* E*-layer critical frequencies for May, June, July, and August 1933.*

Curves represent hourly averages of lowest critical frequencies.

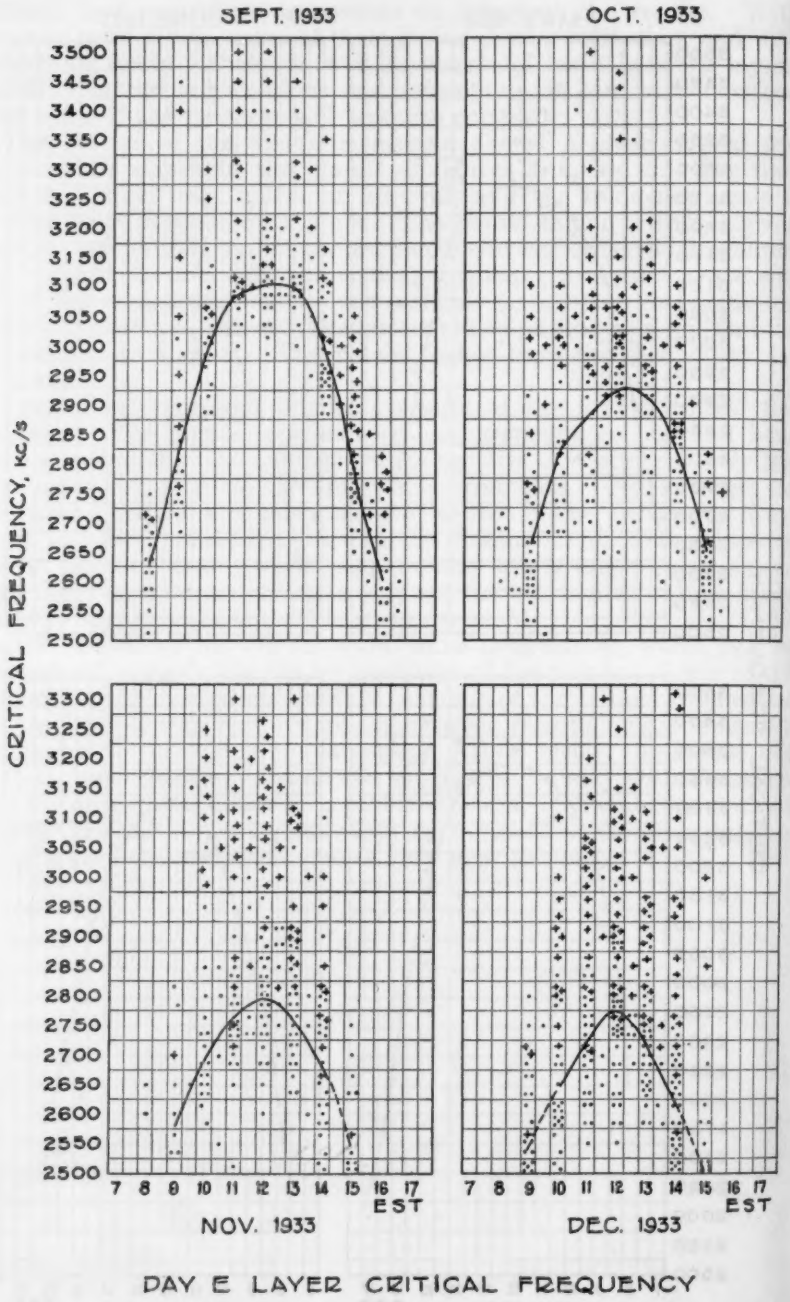

FIGURE 4.—*Daytime E-layer critical frequencies for September, October, November, and December 1933.*

Curves represent hourly averages of lowest critical frequencies.

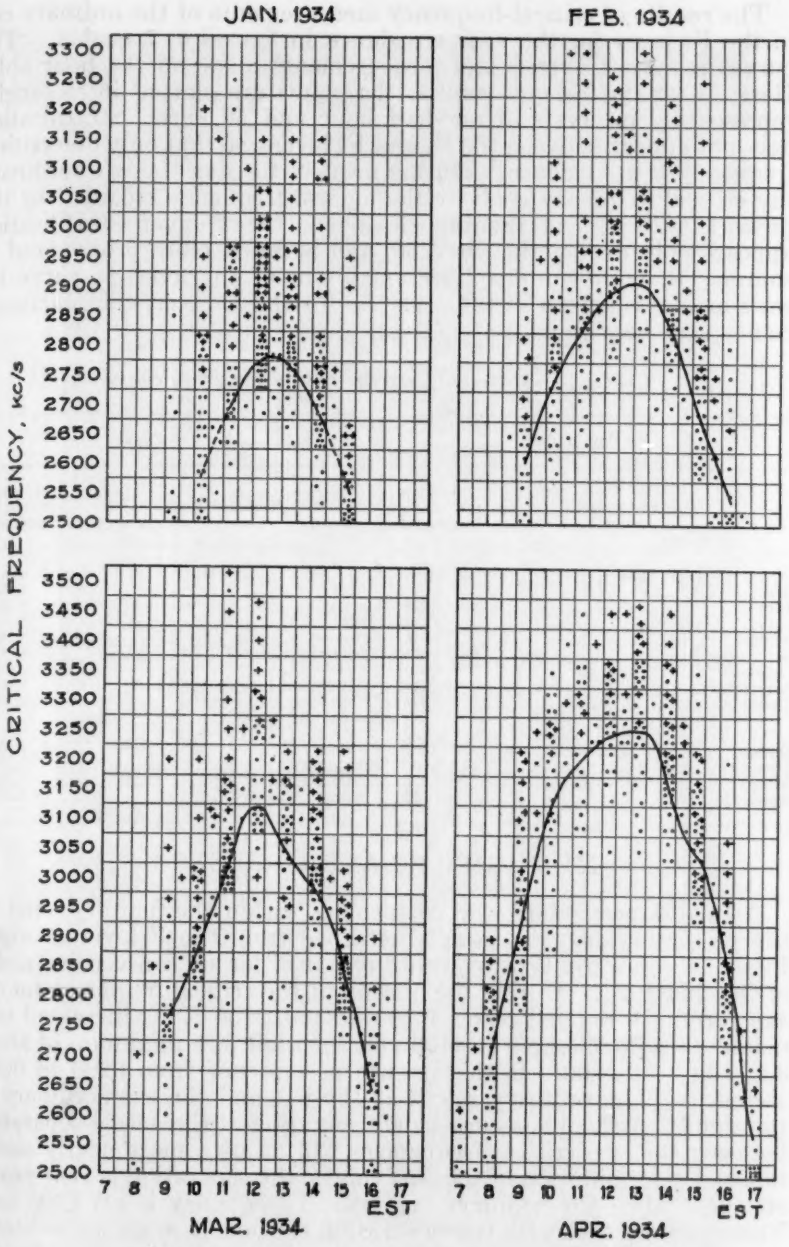

FIGURE 5.—*Daytime E-layer critical frequencies for January, February, March, and April 1934.*

Curves represent hourly averages of lowest critical frequencies.

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The results of critical-frequency measurements of the ordinary ray in the F_1 layer for the year are shown in figures 6, 7, and 8. The curves represent averages of measurements made on the hour only. Here, as for the E-layer results, the points are plotted in rectangles representing intervals of one-half hour and 50 kc/s. Stratification does not appear between the F_1 and F_2 layers, so that only one critical frequency is in evidence. During most of the day the extraordinary ray critical frequency is above the highest frequency recorded by the present system. As mentioned above, the F-layer stratification appears only during the daytime, and is much more pronounced in summer than in winter. The maximum of the average curve for each month is shown in table 1. As for the E layer, the maximum comes very near to noon.

TABLE 1.—*Maxima of average critical frequency curves*

For day E layer		For day F layer	
Year and month	Average critical frequencies	Year and month	Average critical frequencies
1933	kc/s	1933	kc/s
May	3,270(?)	May	4,205(?)
June	3,230(?)	June	4,205(?)
July	3,375(?)	July	4,205(?)
August	3,310	August	4,160
September	3,105	September	4,175
October	2,925	October	4,050
November	2,795	November	3,980
December	2,775	December	3,870
1934		1934	
January	2,780	January	3,850
February	2,910	February	4,115
March	3,120	March	4,215
April	3,255	April	4,275

III. NIGHT F LAYER RESULTS

As mentioned before, the frequencies within the band covered by the present system are usually returned from the F layer at night. Figure 9 shows the type of record obtained for six consecutive nights in October 1933. During the first night the critical frequency for the extraordinary ray fell below 2,500 kc/s at 2000 EST, increased to a maximum of 3,920 kc/s at 0400 and then fell to a minimum of about 3,750 kc/s at 0600. Both rays are in evidence from 0200 to 0600, inclusive. The ordinary ray is at the left and the extraordinary at the right. Although accurate determination of the actual separation between the two critical frequencies will await a more nearly simultaneous determination of the two values, the separation is very nearly 800 kc/s when the ordinary-ray critical frequency is at 2,500 kc/s. Theory shows that with this separation the ions here are undoubtedly electrons. The changes during the second night are quite different. A minimum critical frequency of 3,450 kc/s occurred at 2100 followed by a maximum of 4,100 kc/s at 0000 and another minimum below 2,500 kc/s at 0500. The critical frequency increased also during the other four nights, but it did not fall below 2,500 kc/s unless possibly during the third night when F refractions were obscured by strong sporadic E reflections at 2300 and 0000.

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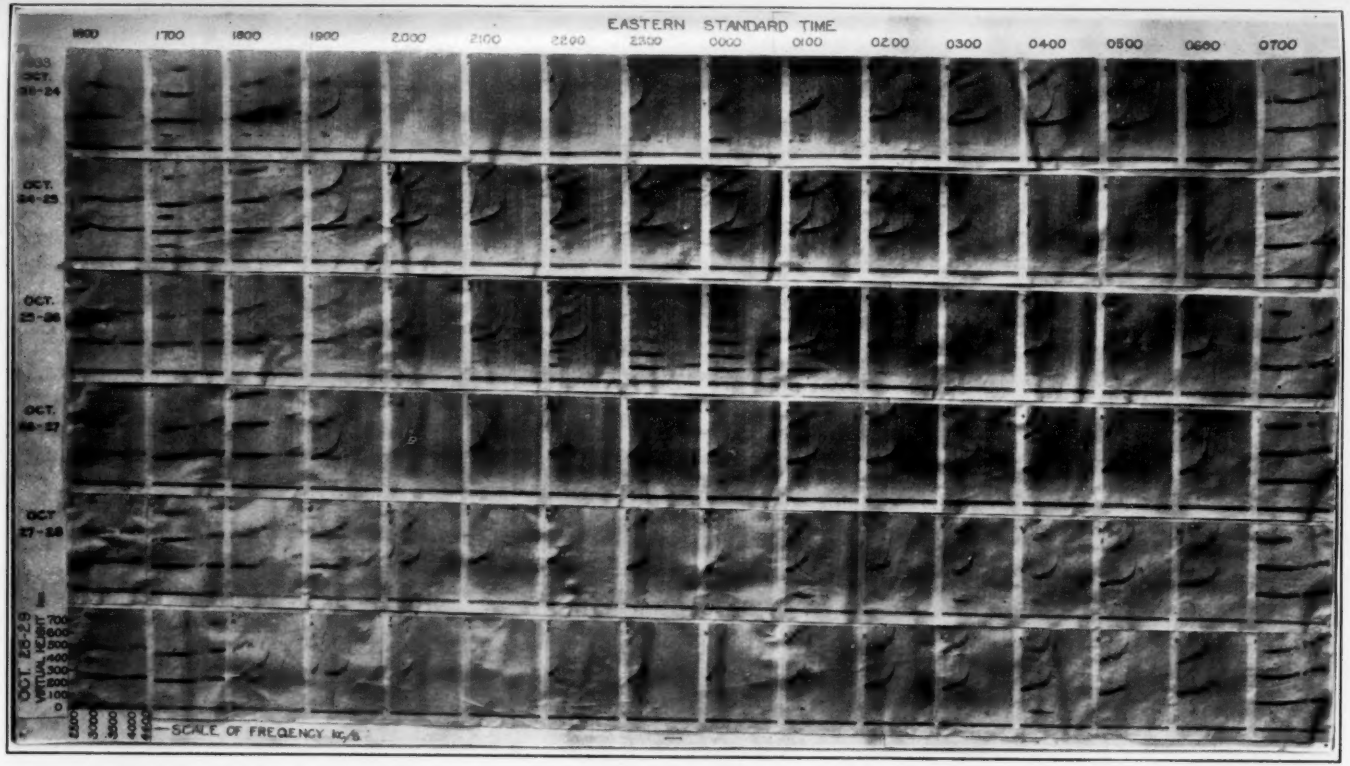

FIGURE 9.—*Records obtained for six consecutive nights in October 1933.*

Note E-layer reflections at 2300 and 0000 eastern standard time during third night.

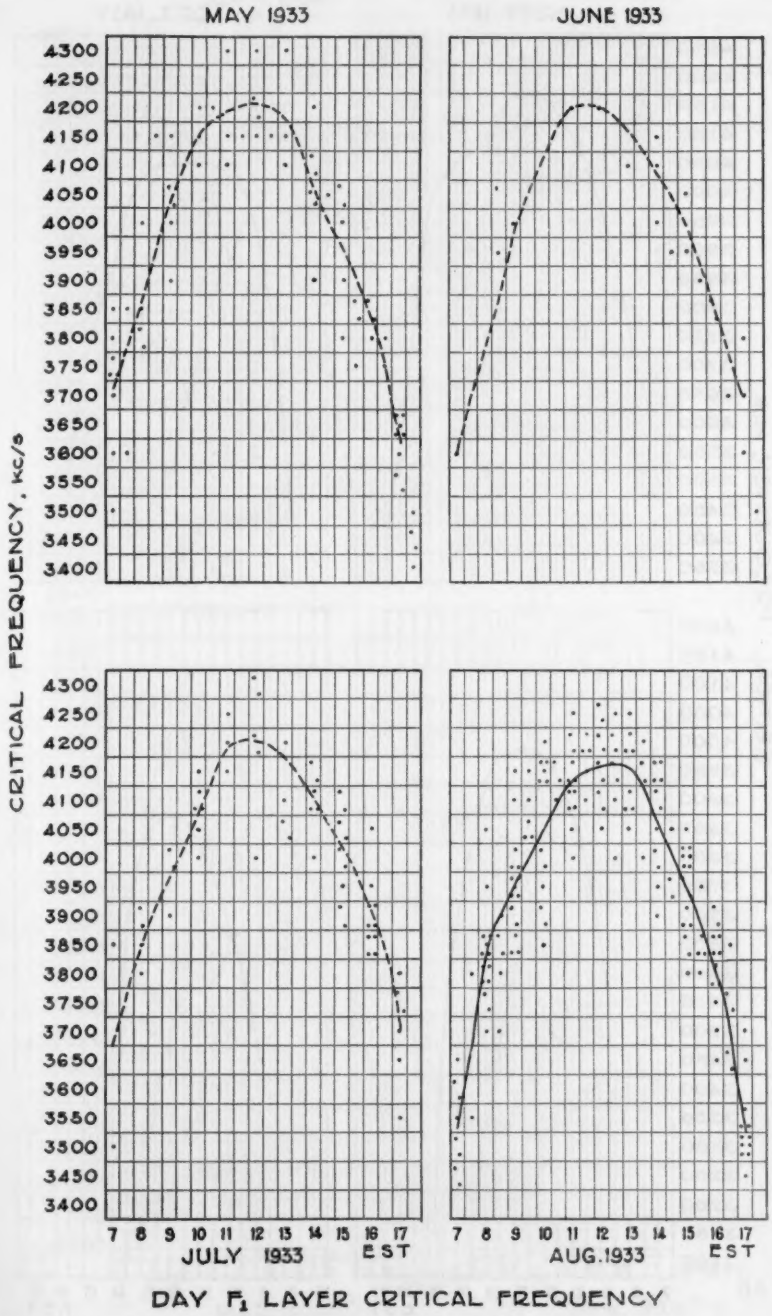

FIGURE 6.—F_1-*layer critical frequencies for May, June, July, and August 1933.*

Curves represent hourly averages.

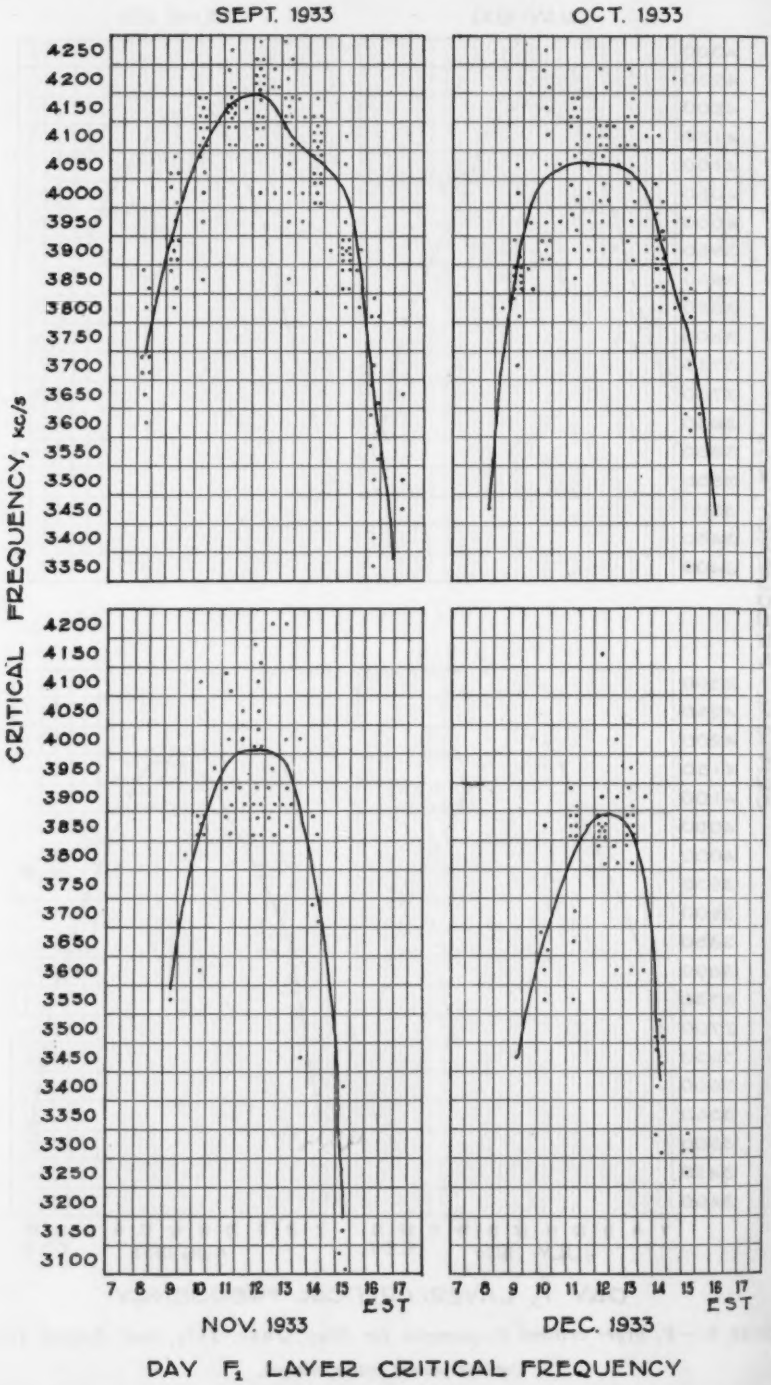

FIGURE 7.—F_1-*layer critical frequencies for September, October, November, and December 1933.*

Curves represent hourly averages.

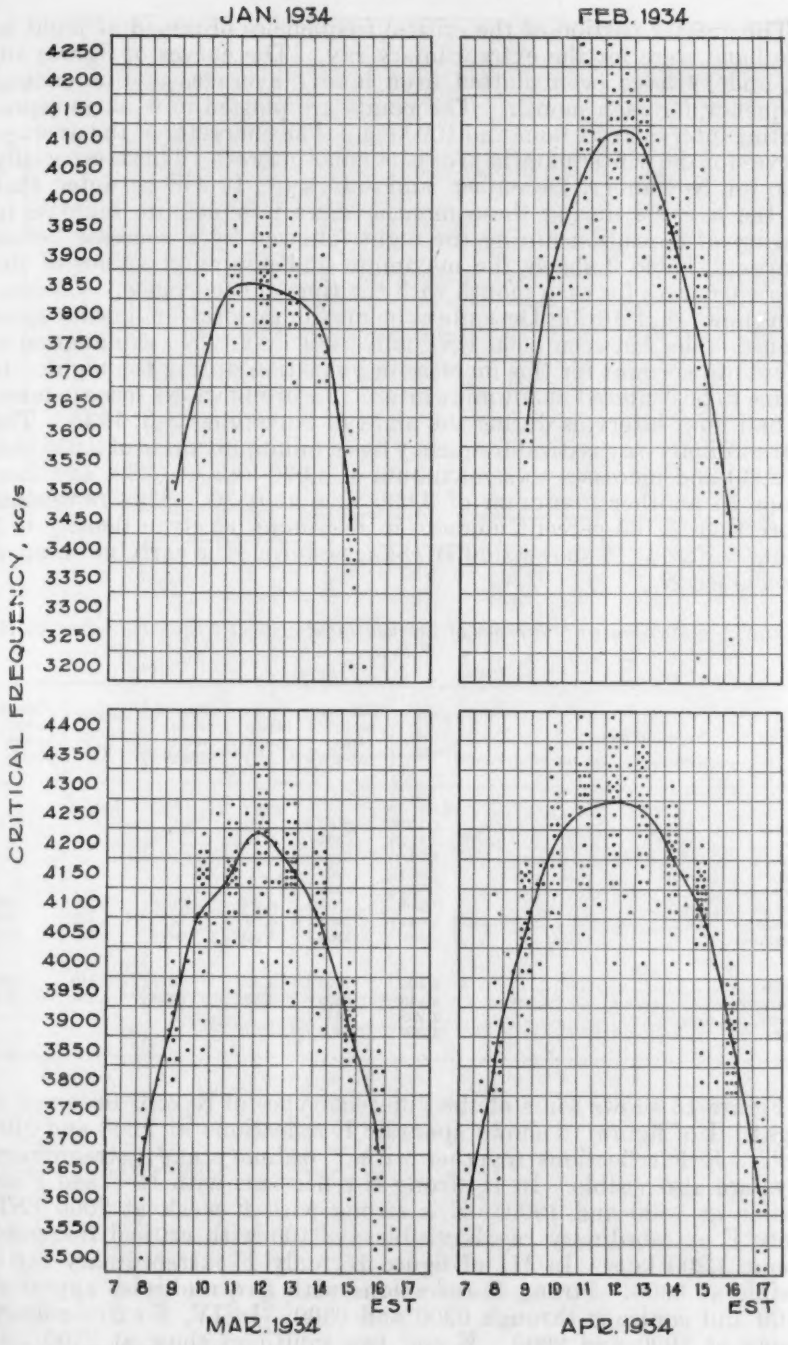

FIGURE 8.—F_1-*layer critical frequencies for January, February, March, and April 1934.*

Curves represent hourly averages.

The greater portion of the critical frequencies obtained at night in this band were for the extraordinary ray. The curves of figures 10, 11, and 12 have been plotted from hourly averages of this critical frequency for each month. The points are plotted in squares representing intervals of 1 hour and 100 kc/s. The character of the average curves for the winter months is of particular interest. This is especially true for November, December, and January. It will be noted that on the average during these months there is a definite increase in density of ionization during the night followed by a decrease before sunrise. Table 2 shows the maximum and minimum values of the average curves for each month with the time of occurrence. Calculation shows that during December the maximum electron density more than doubles between 2200 EST and 0430 EST. No explanation is offered to account for this increase in ionization during the night. It seems to be centered about midwinter. Figure 13 shows records taken at half-hour intervals during the night of November 2–3, 1933. The extraordinary-ray critical frequency has a minimum value of 2,950 kc/s at 2230 and increases to a maximum of 4,070 kc/s at 0330, and then drops to another minimum of 3,030 kc/s at 0530. This represents more than a 100-percent increase in maximum electron density in 5 hours. Figure 14 shows similar changes during the early morning of December 22.

TABLE 2.—*Maxima and minima of average night critical frequency curves for the* F *layer*

Year and month	First minimum,	Time of occurrence EST	Maximum	Time of occurrence EST	Second minimum,	Time of occurrence EST
1933	kc/s		kc/s		kc/s	
May	3,160?	0400				
June	2,735?	0400				
July	2,750?	0400				
August	2,850	0200				
September	2,825	0430				
October	3,330	2300	3,400	0100	3,150	0430
November	3,045	2300	3,830	0320	3,370	0600
December	2,800	2200	3,820	0430	3,430	0600
1934						
January	2,800	2320	3,820	0400	3,440	0600
February	3,045	0000	3,335	0320	3,155	0510
March	3,265	0410				
April	3,010	0400				

Figure 15 shows some of the different types of records obtained at night. I of figure 15 shows sporadic E reflections at 2000 and 2100 EST. E–F reflections together with F ordinary and extraordinary rays are also visible. In II strong E reflections with E–F and F are visible at 1800 and 1900. E is strong with F weak at 2000 EST. Only F extraordinary ray is visible at 2100 with critical frequency about 3,200 kc/s. In III of figure 15, only F extraordinary ray is visible at 0000. Strong E reflections with five multiples appear at 0100 and continue through 0200 and 0300. In IV, F extraordinary shows at 1900 and 2000. E and two multiples show at 2100. At 2200, F extraordinary is visible with E reflection. At this time the E layer appears to be stratified, which is unusual for these conditions. From 2,500 to 3,400 kc/s the virtual height is 120 km, while from 3,400

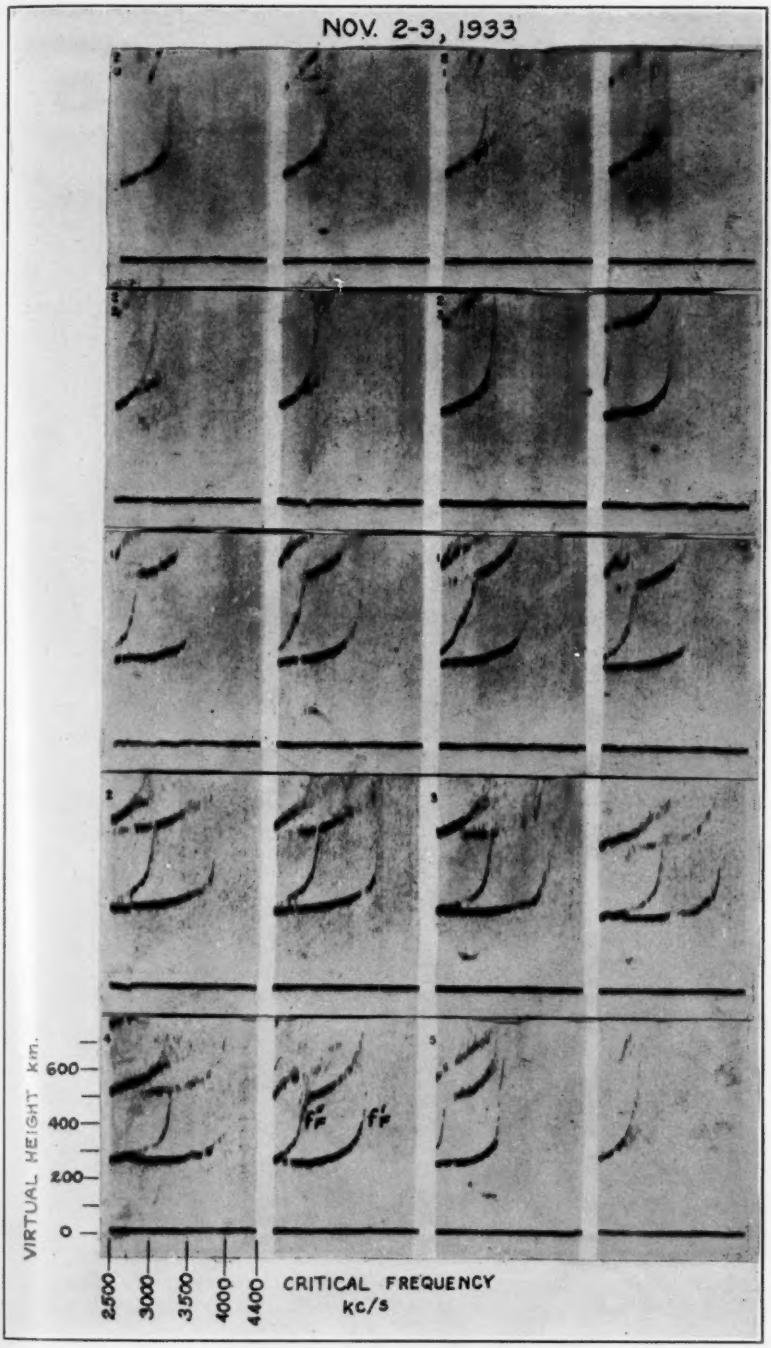

FIGURE 13.—*Records of November 2–3, 1933, showing increase of* F*-layer critical frequency during the night.*

Between 2230 and 0330 the critical frequency for the extraordinary ray increases from 2,950 to 4,070 kc/s, representing more than a 100 percent increase in maximum electron density. f'', represents ordinary ray critical frequency. f', represents extraordinary ray critical frequency.

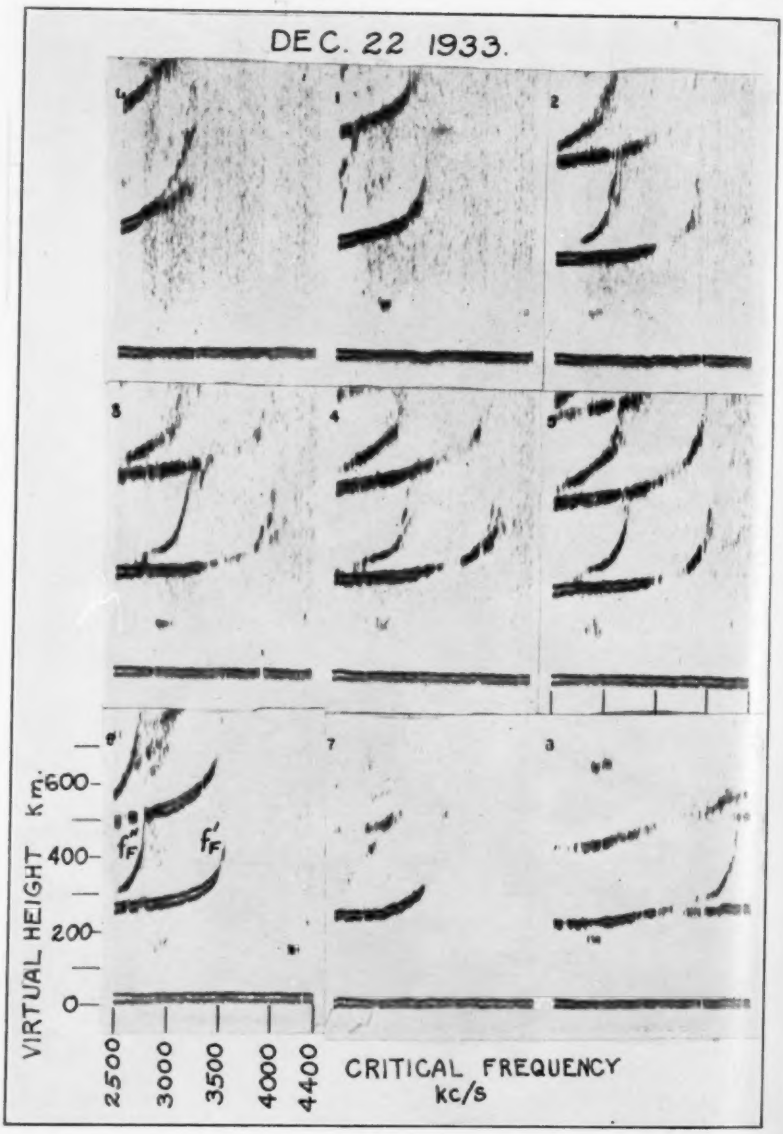

FIGURE 14.—*Records showing increase of* F*-layer critical frequency during the night, December 22, 1933.*

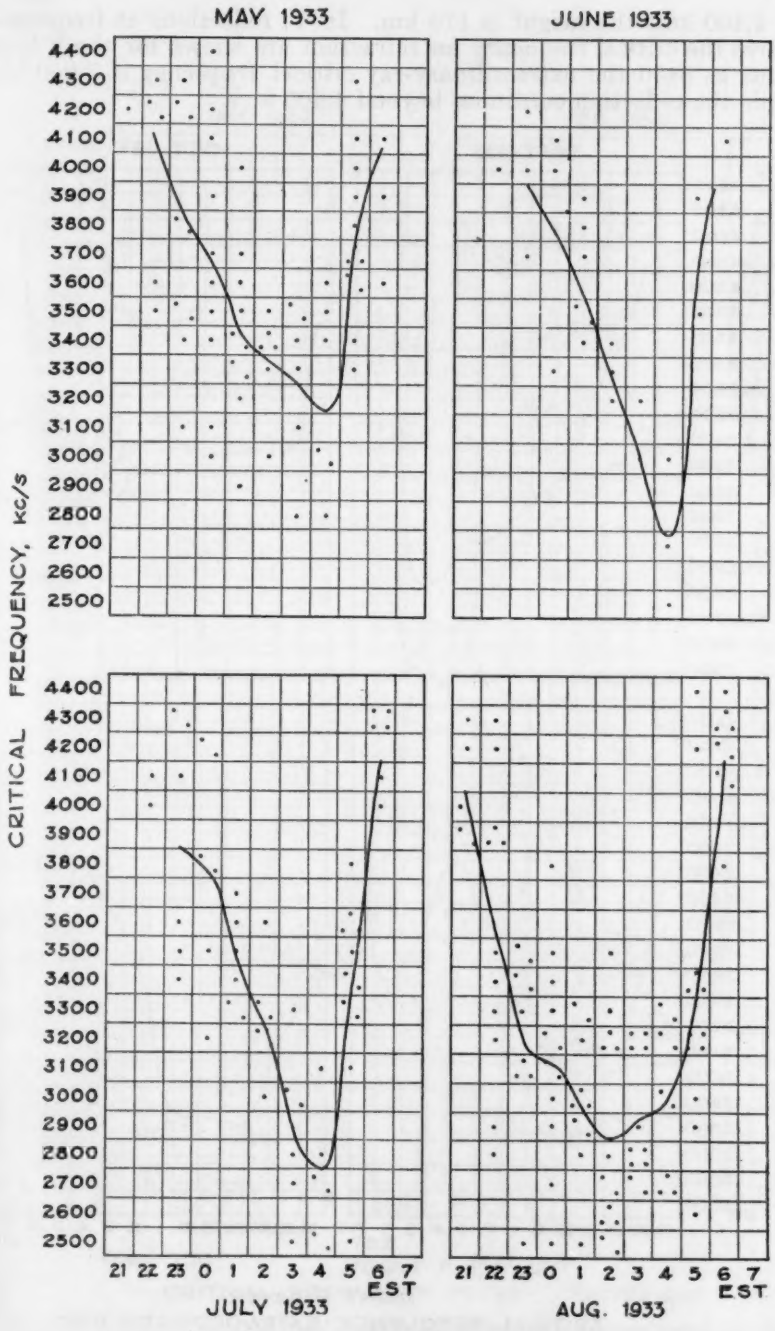

FIGURE 10.—*Night F-layer critical frequencies with hourly average curves for May, June, July, and August 1933.*

to 4,400 kc/s the height is 170 km. In V, reflections at frequencies above the critical frequency for refraction are shown for the F layer. Thus at 0400 the extraordinary-ray critical frequency is 3,950 kc/s, while the reflection continues beyond 4,400 kc/s.

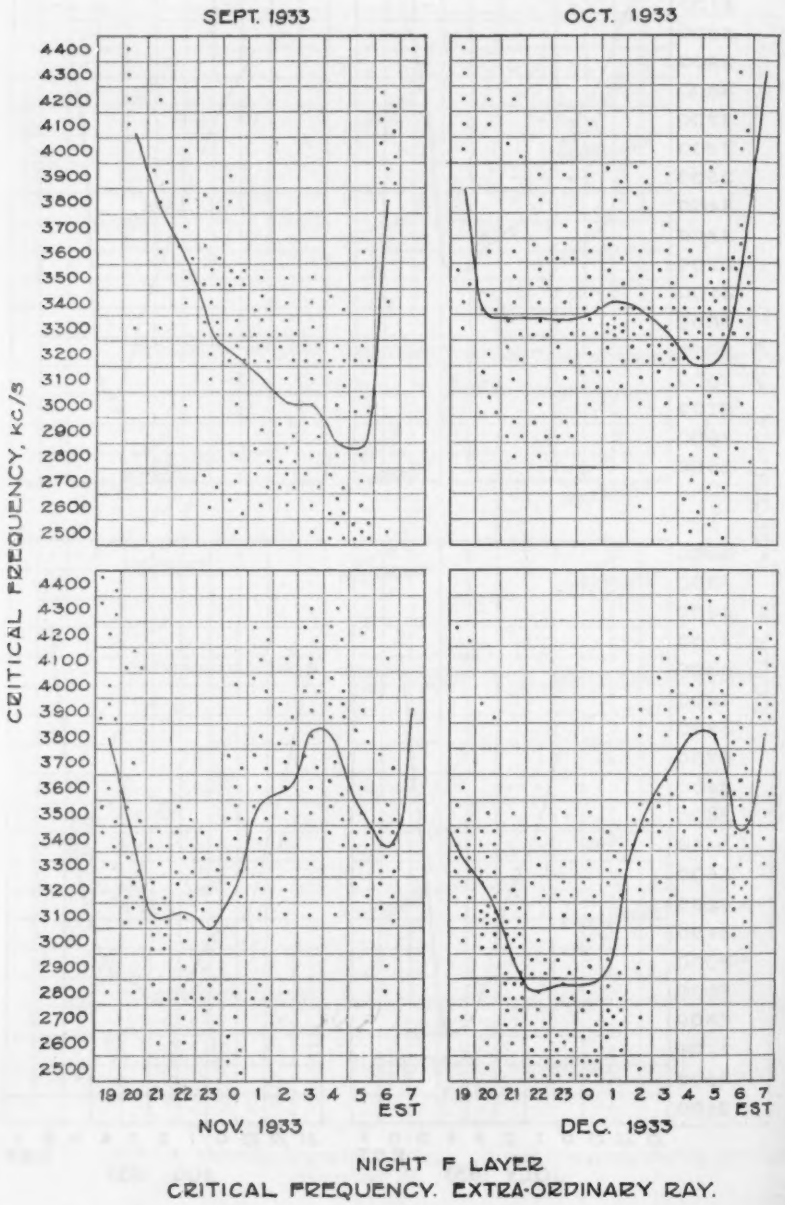

FIGURE 11.—*Night F-layer critical frequencies with hourly average curves for September, October, November, and December 1933.*

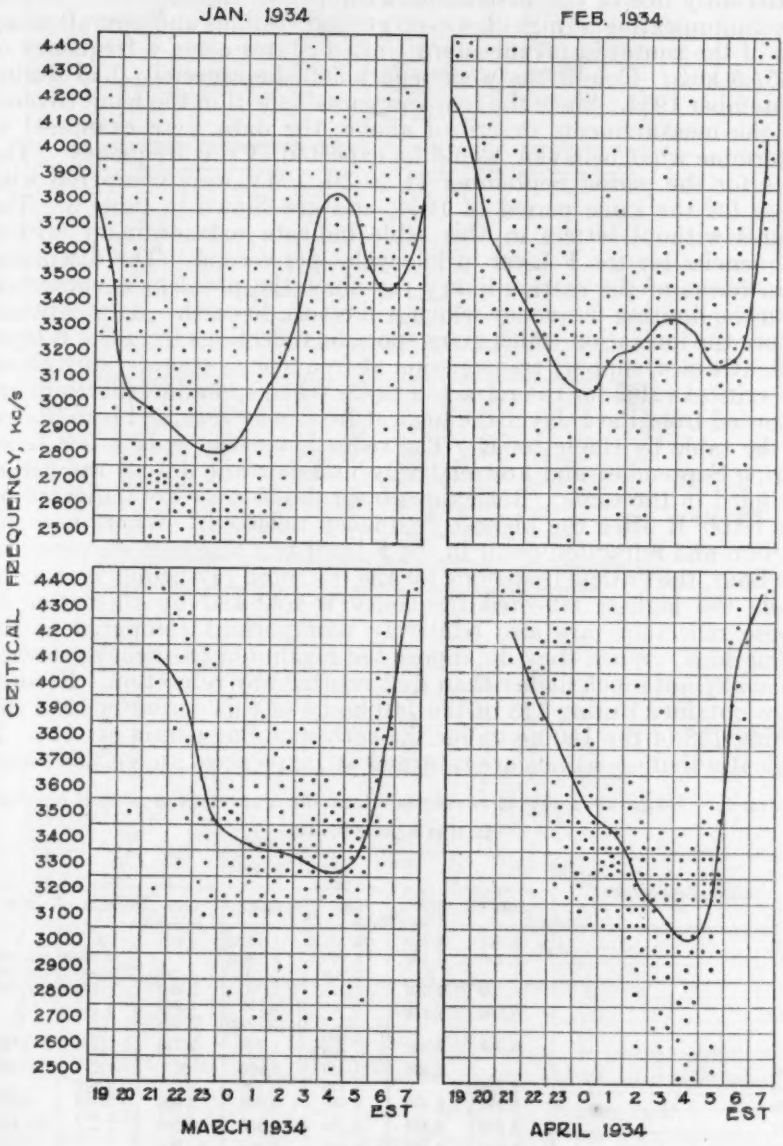

FIGURE 12.—*Night F-layer critical frequencies with hourly average curves for January, February, March, and April 1934.*

IV. APPLICATION OF RESULTS TO A PRACTICAL COMMUNICATION PROBLEM

Recently one of the air-transport companies experienced difficulty in communicating at night between ground stations and aircraft along one of the routes in northeastern United States using a frequency of 3,257.5 kc/s. Conditions were reported to be especially bad during September 1934. Since the frequency used is within the band covered by the measurements described above, the data were examined to determine what behavior would be expected at this frequency. The data for the period September 11 to 30, 1933, were compared with those for the same period of 1934, and are shown in table 3. The figures without letters in this table indicate extraordinary critical frequencies for the F layer in kilocycles per second. The discussion is in terms of the extraordinary ray since the problem is concerned with the limiting frequency which will return to earth. As mentioned before the ionization which gives sporadic reflections from the E layer will, at times, support transmission at frequencies considerably above the critical value for the refracted ray. When sporadic reflections are returned from the E layer the highest frequency returned is indicated in the table by the letter E. The reflections occur only a few times during September and are relatively unimportant during the period included in the table. Reflections from the F layer are indicated by the letter R after the highest frequency reflected. Where both reflection and refraction occur in the F layer two numbers are given for the hour, the critical frequency for the refracted ray being given alone while the highest reflected frequency is followed by the letter R. These reflections are also relatively unimportant compared to the refractions. When they do appear the maximum frequency returned is usually not much higher than that returned by refraction. Records were obtained during 118 of the 140 hours of this period in 1933 and during 138 of the 140 hours for the corresponding period of 1934. X indicates that no signals are returned at frequencies above 2,500 kc/s.

TABLE 3.—*Maximum frequencies returned from the ionosphere at normal incidence*

Sept. 11 to 30, inclusive, 1933

Night, September	Hour, EST						
	2300	0000	0100	0200	0300	0400	0500
11–12	3,220	3,150	3,200R	3,100R	2,600	X	X
12–13	3,250	3,250	3,100R	3,100R	----	2,900R	3,000R
13–14	----	X	2,700	2,770	3,150	3,150	2,600
14–15	2,700	2,550	----	2,700	2,680	2,550	2,530
15–16	2,600	2,550	----	2,710 3,100R	2,700 3,100R	2,620	X
16–17	3,250	3,230	2,800 3,200R	2,770	2,770	2,700	2,720
17–18	----	3,500	3,340	2,930	X	X	E3,900
18–19	2,730	----	2,710	2,740	----	2,610	----
19–20	3,450	3,230	3,230	3,210	2,980	2,700	2,800
20–21	3,330	3,170	3,250	3,130	3,290	E2,900 2,770	E4,400
21–22	3,270	3,100	2,910	2,770	2,900	----	----
22–23	----	----	----	----	----	----	----
23–24	3,350	3,500	3,460	E3,400 3,200	E4,400 3,170	E3,400 3,350	3,220
24–25	3,630	3,500	3,430	3,310	3,150	3,180	3,010
25–26	----	3,530	3,220	2,570	E4,000	E4,400	E3,300 3,180
26–27	----	2,870	2,570	2,730	----	2,970	3,200
27–28	3,770	3,510 2,750R	3,400 3,800R	3,310	3,230	3,150	----
28–29	3,200	3,280	3,180	3,250	3,140	3,090	3,000
29–30	3,080	2,950	2,790	2,910	2,910	3,050	2,970
30–Oct. 1	3,470	3,100	3,150	3,200	3,200	3,270	----
Average	3,220	3,135	3,080	2,955	2,950	2,875	2,840

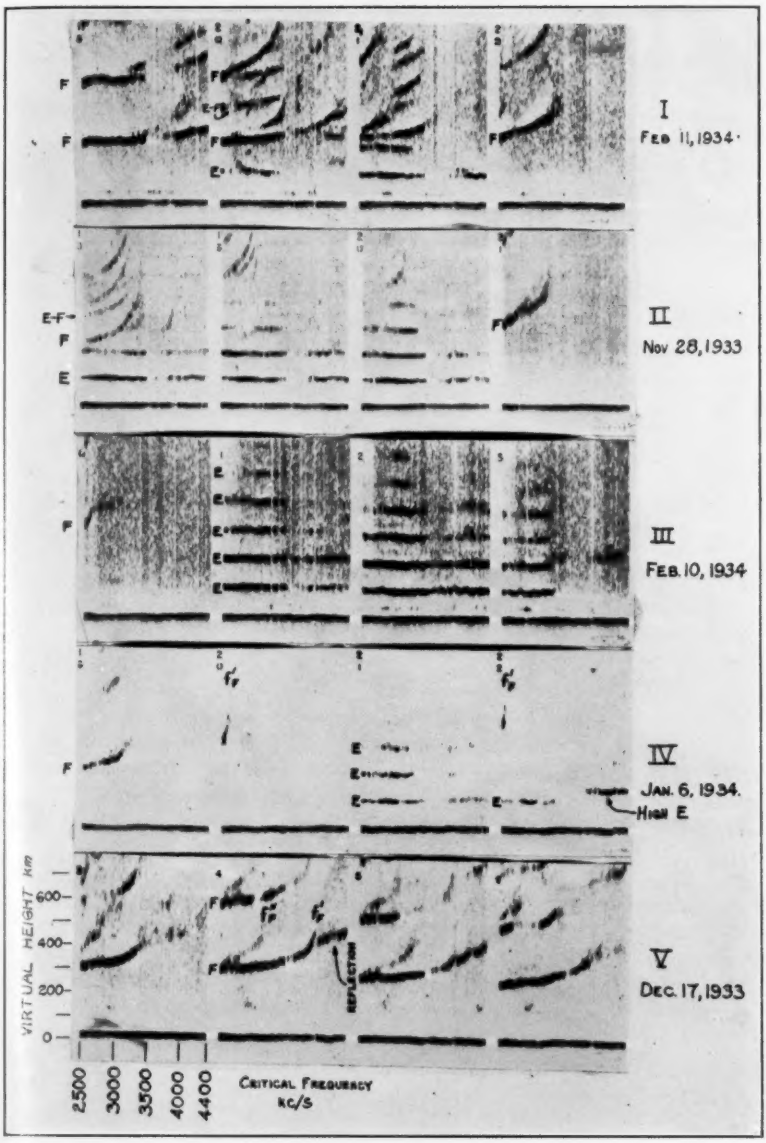

FIGURE 15.—*Different types of records obtained at night.*

I shows sporadic E reflections at 2000 and 2100 eastern standard time. E–F reflections together with F ordinary and extraordinary rays are also visible. II shows strong E reflections with E–F and F at 1800 and 1900. E is strong with F weak at 2000. Only F extraordinary ray is visible at 2100 with critical frequency about 3,200 kc/s. III shows F extraordinary ray at 0000. Strong E reflections with five multiples appear at 0100 and continue through 0200 and 0300. IV shows F extraordinary ray at 1900 and 2000. E and two multiples show at 2100. At 2200 F extraordinary ray is visible with E reflections. At this time E layer appears to be stratified, which is unusual for these conditions. From 2,500 to 3,400 kc/s the virtual height is 120 km, while from 3,400 to 4,400 the height is 170 km. V shows reflections at frequencies above the critical frequency for refraction for the F layer. Thus at 0400 the extraordinary ray critical frequency is 3,950 kc/s while the reflection continues beyond 4,400 kc/s.

TABLE 3.—*Maximum frequencies returned from the ionosphere at normal incidence*—Continued

Sept. 11 to 30, inclusive, 1934

Night, September	Hour, EST						
	2300	0000	0100	0200	0300	0400	0500
11-12		3,900	3,350	2,950	2,770	2,700	2,760
12-13	4,200	4,100	3,900	3,670	3,170		3,000
13-14	4,250	3,950	3,750	3,500 3,900R	3,550 3,800R	3,400 3,800R	3,350 3,800R
14-15	4,500	4,000	3,550	3,400	3,330	3,180	3,200 3,800R
15-16	4,060	3,820	3,600	3,510	3,280	E3,500 3,260	3,060
16-17	4,180	4,050	3,670	3,370	3,000	2,550	X
17-18	3,650	3,700R	3,680R	3,450R	3,500R	3,600R	3,900R
18-19	3,630	3,530	3,650	3,720	3,570	3,600	3,350
19-20	4,000	3,900	3,600	3,330	2,850	2,750	3,100
20-21	3,800	3,500	3,200	3,200	3,000	3,020	2,940
21-22	4,500	4,270	3,650	3,240	2,900	2,760	E2,650 2,770
22-23	3,300	3,050	2,770	2,760	2,720	2,730	E weak 2,800
23-24	3,750	3,600	3,650	3,330	2,950 3,400R	X	3,150
24-25	4,300	4,070	3,870	3,350	3,300	2,700	2,500 3,100R
25-26	E3,500	E3,200	2,800 3,400R	2,870 3,500R	3,300	E3,400 2,950	3,250
26-27	3,650	3,500	3,650	3,830	3,530	3,400	3,320
27-28	3,150	3,130	3,160	3,130	3,180	3,110	E3,700
28-29	3,500	3,380	3,280	3,250	3,300	3,400	3,450
29-30	3,600	3,730	3,650	3,600	3,470	3,580	3,530
30-Oct. 1	3,130	3,000	3,120	E3,000 3,160	E2,950 3,160	3,150	3,200
Average	3,840	3,690	3,470	3,320	3,175	3,040	3,060

The curves of figure 16 are plotted from the hourly averages of the F-layer extraordinary ray critical frequency and may be used together with the lower curve of figure 17 to determine, on the average, the highest frequency which would be expected to be useful for transmission for any short distance between transmitting and receiving stations.

For example, the average critical frequency at 4:00 a. m. during the period September 11 to 30, 1934, is 3,040 kc/s. Then from the lower curve of figure 17 the factor for 100 miles, say, is found to be 1.06 and for 200 miles is 1.21. Then on the average during this period no sky-wave frequencies above $1.06 \times 3,040$, or 3. 225 kc/s, would be received at distances nearer than 100 miles from the transmitter, and no frequencies above $1.21 \times 3,040$, or 3,680 kc/s, would be received at 200 miles or nearer. The variability from night to night is quite large so that individual values of critical frequency are often much different from the average value. Table 3 shows that the critical frequencies from which the average value was taken for 4:00 a. m. range from 2,700 to 3,600 kc/s. The curves of figure 17 may be used together with table 3 to determine the limiting frequency for any distance at any hour of this period. The upper curve should be used if E reflections occur. The factors given by the curves of figure 17 are simply secants of the angle of incidence at the layer.

It will be noted that the curve for September 1933, shown in figure 16, is somewhat different from that shown in figure 11. This is due to the fact that the curve of figure 11 represents the whole month while the other curve represents only the last 20 days of the month.

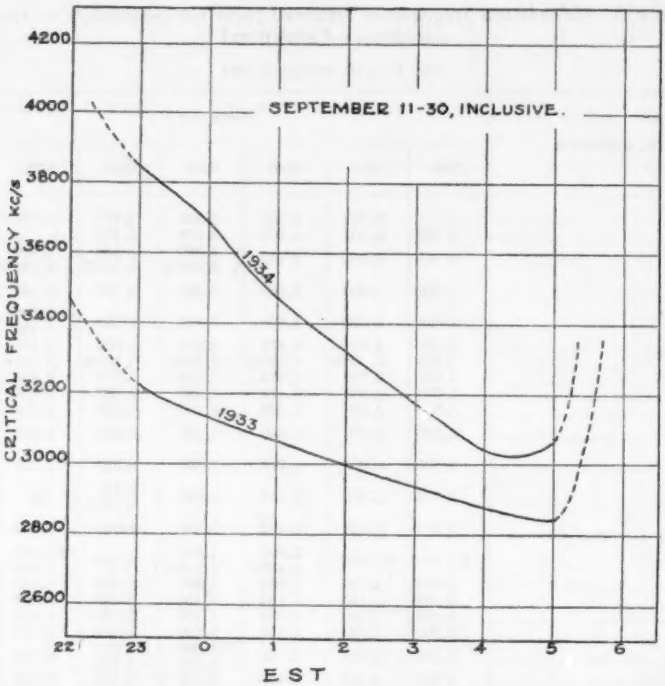

FIGURE 16.—*Hourly averages of night F-layer extraordinary ray critical frequencies for periods September 11 to 30, 1933, and for September 11 to 30, 1934.*

Note that minimum for 1934 is about 180 kc/s higher than for 1933.

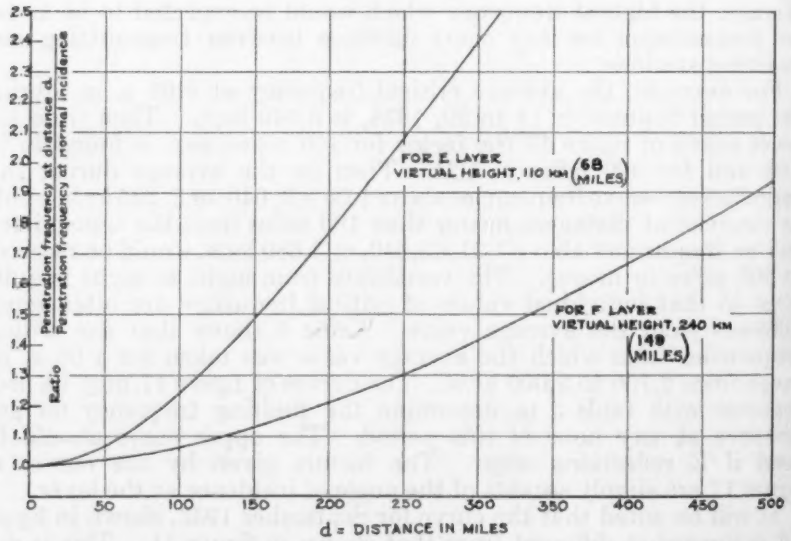

FIGURE 17.—*Approximate multiplying factors for determining limiting frequency of penetration for any distance between transmitting and receiving stations.*

These factors multiply the critical frequencies for normal incidence.

It is interesting to note that the minimum of the average curve for 1934 is about 180 kc/s higher than that for 1933. Since the trend of the sunspot curve is upward it might be inferred that the critical frequencies will increase as the sunspot cycle progresses upward, but since these observations extend over such a short period of time it is not advisable to make any predictions at this time. The provisional sunspot numbers total 57 for this period of September 1933, and 106 for the same period of 1934.

Table 4 is prepared from table 3 and shows the percentages of the time that the critical frequency for the extraordinary ray falls below 2,500, 2,750, 3,000, and 3,250 kc/s during the periods September 11 to 30, 1933 and 1934. The percentages of the time that 2,750, 3,000, and 3,250 kc/s were above the limiting frequency for a distance of 100 miles and, similarly, when 3,000 and 3,250 kc/s were above the limiting frequency for 200 miles, are also given in table 4.

TABLE 4.—*Percentages of the time during the periods Sept. 11 to 30, 1933 and 1934, for which limiting frequencies fell below specified values*

[Data cover hours 2300 to 0500; 11:00 p. m.–5:00 a. m. EST]

f=frequency specified	Critical frequency falls below *f*		*f* exceeds limiting frequency—			
			For 100 miles		For 200 miles	
	1933	1934	1933	1934	1933	1934
kc/s	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
2,500	5.1	1.45				
2,750	25.4	5.8	10.2	2.9		
3,000	44.0	17.4	30.5	12.3	5.1	1.45
3,250	74.5	39.2	46.5	22.4	15.3	2.9

It is likely that the satisfactory ground-wave range at this frequency is only 30 or 35 miles so that transmission is mainly by sky wave. The results of this study show that at times night transmissions over short distances at a frequency of 3,257.5 kc/s pass through the ionosphere and are lost from the earth. The results also indicate that a lower frequency such as 2,750 kc/s passes through the ionosphere at a given angle a much smaller percentage of the time. It would be necessary to go below 2,500 kc/s to obtain practically complete freedom from skipping. The other F-layer critical frequency graphs indicate that transmissions at a frequency of 3,257.5 kc/s will often pass through the ionosphere during any season. These graphs (fig. 10, 11, and 12) together with the lower curve of figure 17, may be used to determine, on the average, the limiting frequency for any time of the year for any distance.

In allocating frequencies for a given type of service a consideration of data of the type shown here should prove useful. World-wide information will be necessary for an intelligent allocation of frequencies to be used in different geographical locations and for different types of service.

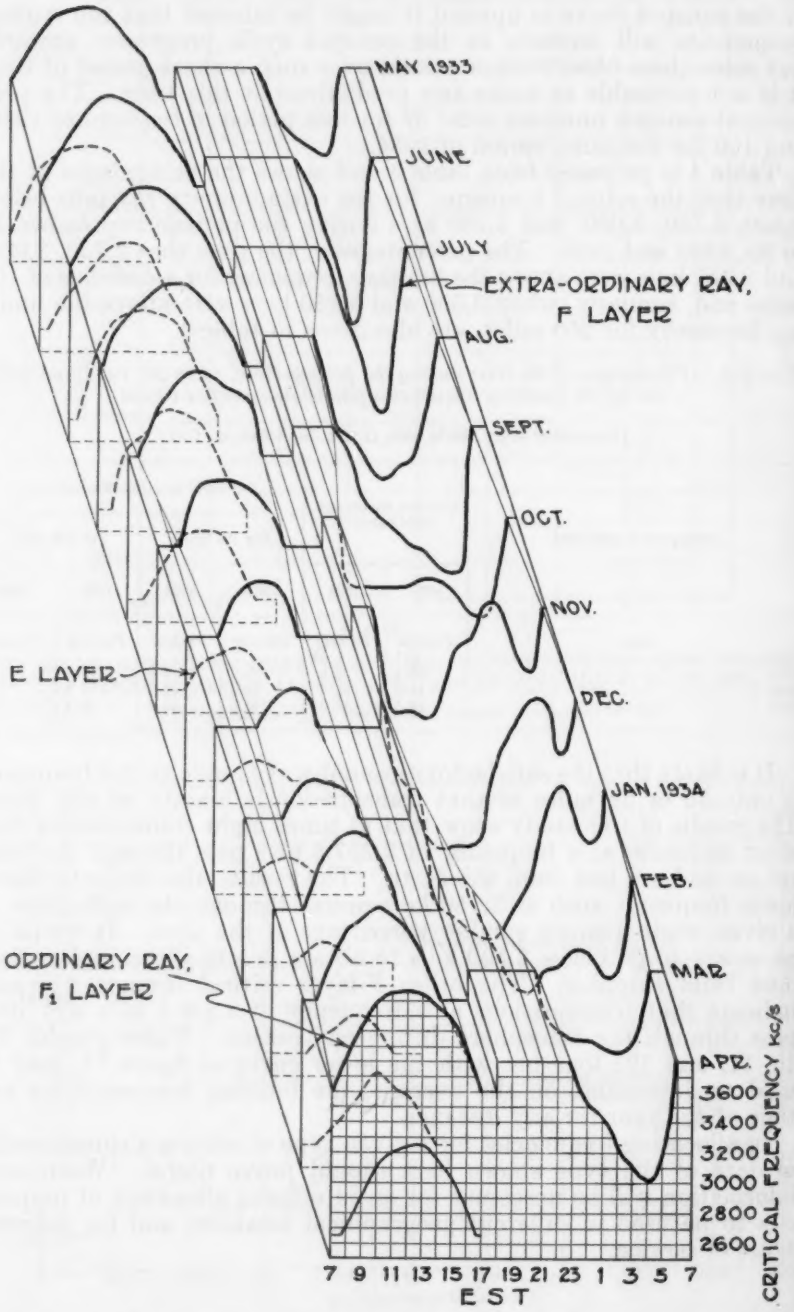

FIGURE 18.—*Solid diagram summarizing daytime* E *and* F_1 *critical frequencies and nighttime* F *critical frequencies for one year.*

V. CONCLUSIONS

An attempt is made to picture the results of the year's critical frequency measurements in the solid diagram of figure 18. The hourly averages of the day F_1 critical frequencies above 3,600 kc/s are shown in the solid curves at the left. The dotted curves below these represent averages of the day E critical frequencies above 2,650 kc/s. The solid curves at the right represent averages of night F critical frequencies below 3,800 kc/s. It is evident that the band used (2,500 to 4,400 kc/s) gives an important and interesting part of the total cross section. The day E and F_1-layer critical frequencies are seen to follow in phase with the sun both diurnally and seasonally. During the winter night the F-layer critical frequency drops until an hour or two before midnight, then increases until about 0400, after which it decreases again before sunrise. The maximum density of ionization frequently more than doubles after the first minimum.

A detailed analysis of the data has not yet been made with relation to magnetic storms. There have been no severe magnetic storms coincident with the hourly observations during the last one and one-half years. Professor Appleton has reported that during magnetic storms in the northern Norway polar region reflections from the ionosphere were absent at all frequencies. No such pronounced effect has been observed in this latitude during the past one and one-half years. It is expected that the severity of magnetic storms will increase with the advance of the sunspot cycle during the next four or five years so that the relation between magnetic storms and changes in the ionosphere will be more easily recognized.

The probable effect of solar disturbances likewise will be demonstrated only by the accumulation of data over a longer period of time. Although the average night F-layer critical frequency curve for September 1934 is considerably higher than that for September 1933, no predictions are made at this time that this indicates a definite trend upward in the future. Data accumulated during the next four or five years should show how much sunspots do affect critical frequencies.

Information of the type shown here should prove useful in the study of the properties of the upper atmosphere as well as in the study of radio transmission.

Although the results obtained give a considerable part of the whole cross section it is desirable to extend the present system so that all of the critical frequencies will be obtained for the 24 hours. When more complete information of this type is available for different parts of the world and when the results are compared with actual transmission data a more complete understanding of sky-wave transmission should follow.

WASHINGTON, December 27, 1934.

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OPTICAL ROTATIONS AND OTHER PROPERTIES OF THE LEAD AND CALCIUM ALDONATES [1]

By Horace S. Isbell

ABSTRACT

The preparation and properties of numerous lead and calcium salts of the aldonic acids are reported. It is shown that the addition of lead salts to the alkaline earth salts of the α-hydroxy acids causes large changes in specific rotation, which follow with striking regularity the configuration of the α-carbon atom in the aldonic acid. Evidence is presented to show that the lead aldonates are acids which can be titrated with standard alkali and that their solutions give rise by hydrolysis to small quantities of the free aldonic acids which undergo lactone formation, causing small changes in rotation.

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I. OPTICAL ROTATIONS OF THE LEAD AND CALCIUM ALDONATES

A comparison of the specific rotations of the salts of gluconic acid [2] shows that the lead and nickel salts are levorotatory, while the sodium, potassium, ammonium, barium, calcium, magnesium, manganese, and zinc salts are dextrorotatory. This suggests that the lead and nickel salts differ fundamentally from the others. On account of this it was decided to investigate other sugar acids in order to determine whether their lead salts also exhibit unusual properties. Some preliminary experiments given in table 1 showed that the addition of lead nitrate to a solution of calcium gluconate caused the optical rotation to change, before readings could be made, from a dextrorotatory to a levorotatory value. This change is in the opposite direc-

[1] A part of the work given in this paper was presented by H. S. Isbell and F. J. Bates before the Division of Sugar Chemistry, American Chemical Society, St. Petersburg, Fla., March 1934.

[2] May, Weisberg, and Herrick. J. Wash. Acad. Sci., **19**, 445 (1929).

tion from that which occurs when ammonium molybdate or uranate is added to calcium gluconate,[3] but it is what might be expected from the optical rotation of lead gluconate. As may be seen from figure 1, the optical rotation varies with the concentration. The molecular rotation of 0.05 molar calcium gluconate containing 0.05 molar lead nitrate is −2,200, whereas the molecular rotation of 0.05 molar lead gluconate is −3,200 and of calcium gluconate +4,200. In other words, the optical rotation of the solution containing equivalent quantities of lead and calcium approaches the rotation of the lead salt, which is evidence that lead gluconate predominates. Presumably the lead ion combines in some manner with the hydroxyl groups of the sugar acid so as to form a complex molecule or ion. The aldonic acids contain several hydroxyl groups which could enter into the formation of complex molecules. The configuration of the lead complex and its optical rotation depend on whether the

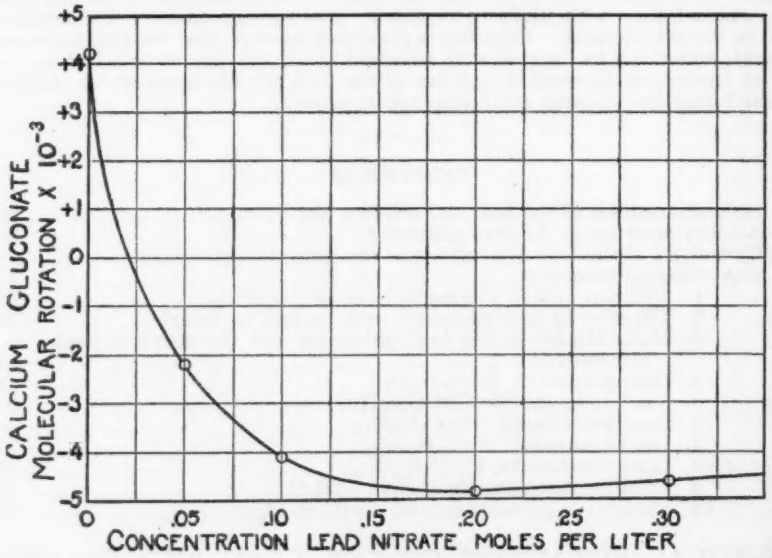

FIGURE 1.—*Changes in optical rotation caused by adding lead nitrate to 0.05 molar calcium gluconate.*

hydroxyl forming the complexion lies to the right or left. Although various metals form complex ions which differ in structure and optical rotation, for a given metal one would expect a correlation between the optical rotation of the complex ion and the configuration of the hydroxyl group involved in its formation.

A comparison of the crystalline lead and calcium salts of the aldonic acids, as given in table 2, reveals a striking regularity between the difference in the optical rotations and the configuration of the α-carbon. *The calcium salts of the aldonic acids are more dextrorotatory than the lead when the hydroxyl group of the α-carbon*

[3] Bennet-Clark. Biochem. J. 28, 45 (1934); also Fisher and Bailey, J. Ass'n. Official Agr. Chem. 15, 461 (1932).

lies to the right, and more levorotatory when it lies to the left. As only a limited number of crystalline lead salts are available for comparison, it is necessary to obtain additional data in order to substantiate this empirical rule.

TABLE 1.—*Changes in the rotation of calcium gluconate caused by the addition of lead nitrate*

Elapsed time	Rotation of calcium gluconate	
	+3.11° S	+3.11° S
	Rotation after addition of—	
	2 g of lead nitrate in 100 ml of solution	6 g of lead nitrate in 100 ml of solution
	°S	°S
5 minutes	−1.30	−3.58
15 minutes	−1.28	−3.53
30 minutes	−1.22	−3.52
60 minutes	−1.21	−3.50

TABLE 2.—*Comparison of the optical rotations of aqueous lead and calcium salts at 20° C*

Substance	Formula	Concentration (g/100 ml)	$[\alpha]_D^{20}$	Molecular rotation [1]	Difference in molecular rotation	Configuration [2]
Calcium gluconate	$Ca(C_6H_{11}O_7)_2.2H_2O$	2.33	+8.80	+4,100	+7,220	+
Lead gluconate	$Pb(C_6H_{11}O_7)_2$	3.12	−5.23	−3,120		
Calcium mannonate	$Ca(C_6H_{11}O_7)_2.2H_2O$	2.33	−7.31	−3,410	−120	−
Lead mannonate	$Pb(C_6H_{11}O_7)_2$	2.99	−5.50	−3,290		
Calcium galactonate	$Ca(C_6H_{11}O_7)_2.5H_2O$	2.56	+.93	+480	+8,190	+
Lead galactonate	$Pb(C_6H_{11}O_7)_2$	.416	−12.90	−7,710		
Calcium xylonate	$Ca(C_5H_9O_6)_2.2H_2O$	2.03	+12.42	+5,050	+8,660	+
Lead xylonate	$Pb(C_5H_9O_6)_2.H_2O$	1.71	−6.50	−3,610		
Calcium arabonate	$Ca(C_5H_9O_6)_2.5H_2O$	2.30	+2.97	+1,340	+4,940	+
Lead arabonate	$Pb(C_5H_9O_6)_2$	.169	−6.70	−3,600		

[1] The product of the specific rotation and the molecular weight of the salt.
[2] When the hydroxyl on the α-carbon lies to the right the configuration is designated with a plus sign.

TABLE 3.—*Change of rotation of salts of aldonic acids caused by addition of* $Pb(NO_3)_2$.

Substance	Rotations for aqueous solutions of various composition			[M]-[M']	Configuration
	Moles per liter of aldonate 0.05		Moles per liter of aldonate 0.05 lead nitrate 0.2		
	$[\alpha]_D^{20}$	[1][M]	[1][M']		
Calcium gluconate, $Ca(C_6H_{11}O_7)_2.2H_2O$	+8.80	+4,100	−4,860	+8,960	+
Magnesium gluconate, $Mg(C_6H_{11}O_7)_2.3H_2O$	+11.30	+5,290	−5,340	+10,630	+
Calcium mannonate, $Ca(C_6H_{11}O_7)_2.2H_2O$	−7.31	−3,410	−1,770	−1,640	−
Calcium galactonate, $Ca(C_6H_{11}O_7)_2.5H_2O$	+.93	+480	−14,230	+14,710	+
Calcium gulonate, $Ca(C_6H_{11}O_7)_2$	+10.87	+4,680	−400	+5,080	+
Calcium altronate, $Ca(C_6H_{11}O_7)_2.3H_2O$	+2.08	+1,010	−11,590	+12,600	+
Calcium allonate (amorphous)		−80	+5,620	−5,700	−
Calcium arabonate, $Ca(C_5H_9O_6)_2.5H_2O$	+2.97	+1,340	−9,540	+10,880	+
Calcium xylonate, $Ca(C_5H_9O_6)_2.2H_2O$	+12.42	+5,050	−7,720	+12,750	+
Magnesium xylonate, $Mg(C_5H_9O_6)_2.3H_2O$	+15.47	+6,320	−7,900	+14,220	+
Calcium α-glucoheptonate, $Ca(C_7H_{13}O_8)_2.3H_2O$	+5.95	+3,240	−5,100	+8,340	+
Calcium β-glucoheptonate (amorphous)	−8.95	−4,410	+11,510	−15,920	−
Calcium rhamnonate (amorphous)	+13.46	+5,360	+3,360	+2,000	+
Calcium lactobionate (amorphous)	+27.00	+20,370	+18,330	+2,040	+

[1] The specific rotation times the molecular weight of the original salt.

Attention was directed above to the fact that on adding lead nitrate to calcium gluconate the optical rotation approaches that of lead gluconate. Thus it is apparent that information may be obtained indirectly by measuring the changes in optical rotation which occur after adding lead nitrate; in this way lead aldonates are formed in solution and measurements can be made, even though the crystalline salts are not known. The results obtained in this manner with salts derived from twelve aldonic acids are given in table 3. In each case the difference in the optical rotations agrees with the lead-salt rule enunciated above. Since the probability of the occurrence of this regularity without a directing influence is remote, probably the α-hydroxyl group is involved, perhaps by giving rise to strongly optically active coordination compounds with lead. The remaining hydroxyl groups and other factors such as ionization, association, and hydrolysis undoubtedly contribute to the changes in rotation and give rise to the variations in the numerical values. The proportions of the complex ions in solution may be small and vary widely, so that the molecular rotations should not be regarded as true molecular rotations but rather as comparable measures of the optical rotations in the equilibrium states. The optical rotations of the alkaline earth salts in which the hydroxyl groups on the alpha and beta carbons lie on opposite sides, with the exception of calcium lactobionate, appear to be affected more by the addition of lead nitrate than those in which the hydroxyl groups lie side by side. The much smaller effect of lead nitrate on the optical rotation of calcium lactobionate is surprising but not inimical. The large lactobionic acid molecule contains a second grouping, the glycosidic and the adjacent hydroxyl, which is capable of coordination with lead ions. On account of this complication the lead salt rule may not apply to all bionic acids.

II. ACIDIC PROPERTIES OF THE LEAD ALDONATES

As may be seen from the pH titration curve given in figure 2, lead gluconate is a definite acid requiring one equivalent of alkali for neutralization. This might be explained by the following equation:

$$2Pb(C_6H_{11}O_7)_2+Ba(OH)_2\longrightarrow Ba(C_6H_{11}O_7)_2+2PbOH(C_6H_{11}O_7).$$

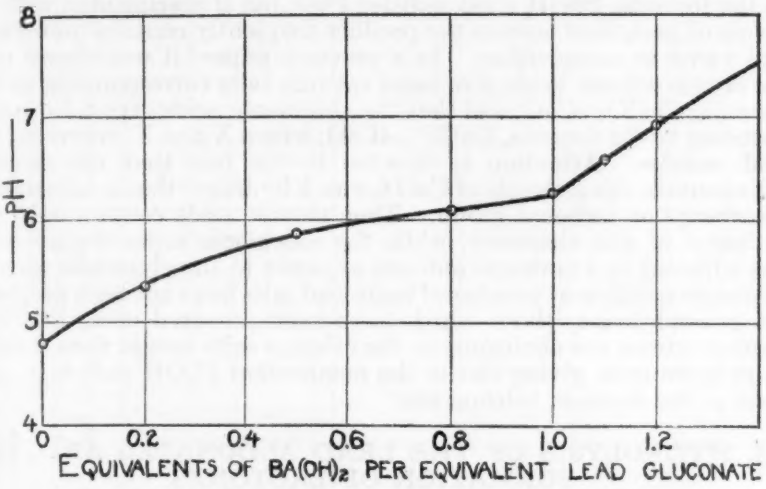

FIGURE 2.—*N/20 lead gluconate containing barium hydroxide.*

Yet the reaction is not as simple as the equation indicates because lead tends to form complex molecules, especially with hydroxy acids.[4] If the lead were combined with the carboxyl and hydroxyl groups by means of primary and secondary valence bonds, as given by the formula below, then the hydrogen atoms marked with positive signs might

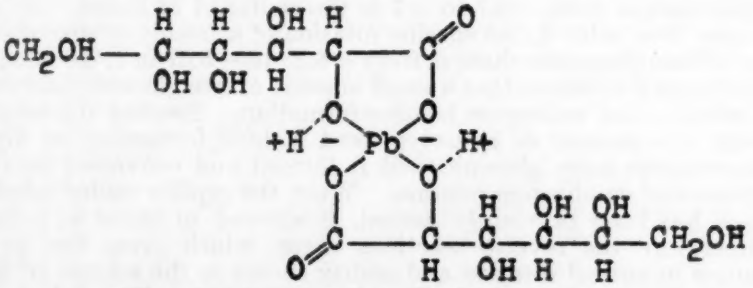

FIGURE 3.—*Hypothetical structure of lead gluconate.*

be considered as the cations of a substituted plumbous acid. One might expect the acid to require two equivalents of alkali for neutralization, but it is well known that only one[5] of the two hydrogen atoms in plumbous acid is readily replaced by metals. The plumbous acid structure, while hypothetical, resembles other similar structures, such

[4] Jellinck and Gordon. Z. phys. Chem. **112**, 207 (1924).
[5] Hantzsch. Z. Anorg. Chem. **30**, 312 (1902).

as the imidoauric acids,[6] and adequately accounts for the marked acidity, in harmony with the chemistry of the hydroxy acids and of lead.

When slightly more than one equivalent of alkali is added to a solution of lead gluconate a difficultly soluble basic salt separates. It appears that sugar acids generally form similar compounds. If prepared in the manner described for basic lead gluconate they correspond to the formula, PbOH (acid radicle) PbO; but if precipitated with an excess of basic lead acetate the product frequently contains more lead and varies in composition. In a previous paper[7] it was shown that the simple aldonic acids give basic calcium salts corresponding to the formula, $Ca(X)_2.2CaO$, and that the aldobionic acids give salts corresponding to the formula, $Ca(X')_2.4CaO$, where X and X′ represent the acid radicles. Attention is directed to the fact that the calcium salts contain one molecule of CaO for each hydroxyl that is adjacent to a carboxyl or carbonyl group. Thus aldonic acids contain only one hydroxyl of this character, while the aldobionic acids contain two, one adjacent to a carboxyl and one adjacent to the glycosidic carbon. Although a sufficient number of basic lead salts have not been prepared for generalization, those which have been prepared using low lead concentrations are analogous to the calcium salts except that there is more hydrolysis, giving rise to the monovalent PbOH radicle in contrast to the divalent calcium ion.

III. HYDROLYSIS OF THE LEAD ALDONATES AND THE FORMATION OF LACTONES

It may be seen from table 1 that the optical rotation of a reaction mixture containing lead gluconate prepared by adding lead nitrate to a solution of calcium gluconate, exhibits a small but definite mutarotation. Measurements with numerous lead aldonates have revealed that similar changes are given by other lead salts and that they resemble the mutarotations of the sugar acids. As previously shown by Rehorst[8] the specific rotation of pure gluconic acid dissolved in water changes from −6.7 to +7 in the course of 24 hours. As may be seen from table 4, the specific rotation of a freshly prepared solution of lead gluconate changes from −5.23 to −5.07 in 1,440 minutes; the change is evidence that a small amount of free gluconic acid exists in solution and undergoes lactone formation. Heating the solution affects the amount of hydrolysis and lactone formation; at higher temperatures more gluconic acid is formed and converted into the lactone-acid equilibrium mixture. When the rapidly cooled solution, which has been previously heated, is allowed to stand at a lower temperature the reverse reactions occur, which gives rise to the changes in optical rotation and acidity shown in the column of table 4 marked "heated sample." The changes in the specific rotations and hydrogen ion concentrations of aqueous lead xylonate, mannonate, arabonate, and galactonate, on heating and standing, also agree with what might be anticipated if more hydrolysis and lactone formation occur at higher temperatures. The reactions are complex, in that equilibrium is established with at least the lead salt and the free acid, and between the acid and its γ- and δ-lactones. Probably the specific

[6] Kharasch and Isbell. J. Am. Chem. Soc. **53**, 3059 (1931).
[7] BS J. Research **11**, 649 (1933) RP613.
[8] Ber. Deut. Chem. Ges. **61**, 163 (1928).

TABLE 4.—*Specific rotations and pH values of saturated solutions of lead aldonates at 20° C*

TABLE 4.—*Specific rotations and* pH *values of saturated solutions of lead aldonates at 20° C*

Time	Lead gluconate 3.123 g $Pb(C_6H_{11}O_7)_2$ per 100 ml				Lead mannonate 3.657 g $Pb(C_6H_{11}O_7)_2$ per 100 ml				Lead galactonate 0.4160 g $Pb((C_6H_{11}O_7)_2$ per 100 ml				Lead arabonate 0.1689 g $Pb(C_5H_9O_6)_2$ per 100 ml				Lead xylonate 1.706 g $Pb(C_5H_9O_6)_2 \cdot H_2O$ per 100 ml			
	Freshly prepared sample		Heated sample		Freshly prepared sample		Heated sample		Freshly prepared sample		Heated sample		Freshly prepared sample		Heated sample		Freshly prepared sample		Heated sample	
	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH	$[\alpha]_D^{20}$	pH
Minutes																				
10	−5.23	4.65	−2.81	4.90	−5.93	4.5	−3.25	5.3	−12.9	5.3	−15.6	5.7	−6.7	5.4	−11.2	5.9	−6.50	4.8	−2.81	5.2
60	−5.12	------	−3.52	------	−5.80	------	−3.68	------	------	------	------	------	------	------	------	------	−6.58	------	−3.48	------
120	−5.18	------	−3.96	------	−5.59	------	−3.91	------	------	------	------	------	------	------	------	------	−6.70	------	−3.63	------
180	−5.15	------	−4.20	------	−5.55	------	−4.04	------	------	------	------	------	------	------	------	------	−6.38	------	−4.06	------
1,440	−5.07	------	−4.97	------	−5.29	------	−4.87	------	−13.3	5.5	−13.9	5.5	−7.8	5.6	−6.06	4.9	−6.06	4.9	−5.88	4.9
2,880	−5.05	4.72	−5.01	4.72	−5.20	5.5	−5.12	5.4	------	------	------	------	------	------	------	------	------	------	------	------

rotations of salts of weak bases in general vary according to concentration, time, and temperature in manner analogous to that disclosed for the lead salts, and possibly some of the numerous discrepancies in the specific rotations of the various salts, recorded in the literature, may be due to these factors.

IV. EXPERIMENTAL PROCEDURE

1. ADDITION OF LEAD NITRATE TO CALCIUM GLUCONATE

The optical rotation of a solution of calcium gluconate (saturated at 20° C) was measured in a 4-dm tube on a Bates saccharimeter and recorded in table 1 as the "rotation before adding lead nitrate." To 100 ml of this solution 2 g of chemically pure crystalline lead nitrate was added and optical rotation measurements made at 20° C. Each reading given in table 1 is the average of several on both sides of the recorded time. The results show that lead gluconate is formed very rapidly; that is, before the first readings could be made. The results given in figure 1 were obtained by similar experiments in which the amount of lead nitrate was varied. Only the initial rotations are reported, as the variation with time is essentially the same for each sample.

The measurements reported in table 2 were made with a saccharimeter, using the conversion factor 0.3462. The samples of calcium gluconate, galactonate, mannonate, and altronate were heated slightly in order to bring the salt into solution. Heat was not applied to bring the lead salts into solution because heating causes changes in their optical rotations. Low concentrations of lead galactonate and arabonate were used on account of their low solubility.

The effect of adding lead nitrate to the various salts given in table 3 was determined essentially as described for the experiments given in table 1. In each case two solutions were prepared and read as soon as a clear solution was obtained. Pure crystalline salts were used with the exception of calcium β-glucoheptonate, calcium lactobionate, calcium rhamnonate, and calcium *l*-allonate; these were prepared by digesting the corresponding lactones with an excess of calcium carbonate. The concentration of salt was estimated from the amount of calcium in solution after removing the excess calcium carbonate by filtration.

2. TITRATION OF LEAD GLUCONATE WITH BARIUM HYDROXIDE

Samples of lead gluconate containing 1.4934 g in 50 ml of water were placed in 100-ml flasks containing sufficient standard barium hydroxide to give the desired concentrations. The quantities of barium hydroxide added are represented by the points on the curve in figure 2. After diluting the solutions to 100 ml with freshly boiled distilled water, the pH was determined electrometrically with a quinhydrone electrode and checked by colorimetric measurements. At about pH 7 a precipitate of basic lead gluconate begins to form. On adding more alkali it dissolves, giving a clear solution at about pH 10. This requires about 1.8 equivalents of alkali.

3. MUTAROTATION OF THE LEAD ALDONATES AND THE EFFECT OF HEAT TREATMENT

Six grams of finely powdered lead gluconate, mannonate, galactonate, arabonate, or xylonate was added to 150 ml of water at 20° C. After shaking 10 minutes the excess lead salt was separated by filtration. The optical rotations and pH measurements recorded in table 4 in the columns headed "Freshly prepared sample" were obtained with the resulting filtrate; time was measured from the beginning of the filtration. After completing the measurements the unused portion of the solution was placed in a glass tube and heated in a boiling water bath for 10 minutes. Then it was cooled rapidly to 20° C and the measurements recorded under the "Heated sample" were made, for which time was taken from the moment when the tube was removed from the boiling water bath.

The optical rotations were converted to specific rotations in the usual manner. The concentration of the salt was calculated from the amount of lead in solution, which was determined by precipitation as lead chromate. The values for the concentrations represent the initial solubilities of the salts in water at 20° C.

4. LEAD GLUCONATE, $Pb(C_6H_{11}O_7)_2$

Lead gluconate was made from gluconic acid and lead carbonate essentially as prepared by May, Weisberg, and Herrick.[9] At 20° C about 3.1 g of the salt dissolved in 100 ml of water in 10 minutes; on standing slightly more salt dissolved. The specific rotation (−5.2) of the freshly prepared aqueous solution, containing 3.123 g of lead gluconate per 100 ml, was slightly less than that found by May, Weisberg, and Herrick (−7.2), but as noted in this paper, different values are obtained by using different concentrations and experimental conditions. *Analysis:* Calculated for $Pb(C_6H_{11}O_7)_2$: Pb, 34.69. *Found:* Pb, 34.72.

Basic lead gluconate, $Pb(CaH_{11}O_7)_2.3PbO.H_2O$, was obtained by adding 125 ml of *N*/10 $Ba(OH)_2$ to 100 ml of *N*/10 lead gluconate. The resulting precipitate was separated by filtration, washed with water, and dried to constant weight at 60° C in vacuo. *Analysis:* Calculated for $Pb(C_6H_{11}O_7)_2.3PbO.H_2O$: Pb, 64.50 *Found:* Pb, 64.55.

5. LEAD XYLONATE, $Pb(C_5H_9O_6)_2.H_2O$

Lead xylonate was prepared first by the method of Hasenfratz.[10] Larger quantities were then prepared from barium xylonate obtained by oxidizing xylose electrolytically in the presence of barium carbonate and barium bromide essentially as described [11] for the preparation of calcium xylonate. The barium in the electrolyzed solution was removed by an equivalent quantity of sulphuric acid and the resulting hydrobromic and xylonic acids were neutralized with normal lead carbonate. After separating the insoluble lead bromide from the more soluble lead xylonate the solution was concentrated and seeded with lead xylonate. After standing several hours a good yield of the lead salt was obtained.

[9] May, Weisberg, and Herrick. J. Wash. Acad. Sci., **19**, 445 (1929).
[10] Compt. Rend. **196**, 350 (1933).
[11] Isbell and Frush. BS J. Research **6**, 1145 (1931) RP328.

Lead xylonate crystallizes so readily that it may be prepared also by adding lead nitrate (20 g in 50 ml of water) to a concentrated solution of magnesium xylonate (25 g in 50 ml of water) followed by alcohol until the solution becomes slightly turbid. After seeding, about 15 g of crystalline lead xylonate can be separated. The product recrystallized from hot water gives, in 2 percent aqueous solution, $[\alpha]_D^{20} = -6.8°$, in agreement with the value reported by Hasenfratz; but the optical rotation varies with concentration and changes slightly when the solution is heated or allowed to stand.

Aqueous solutions of lead xylonate react definitely acid and combine with bases in much the same manner as lead gluconate. A precipitate of basic lead xylonate corresponding to the formula, $Pb(C_5H_9O_6)_2.3PbO.H_2O$, is obtained when lead xylonate is treated with slightly more than one equivalent of dilute barium hydroxide. The basic salt dissolves in an excess of alkali or in the presence of considerable calcium or magnesium xylonate.

6. LEAD GALACTONATE, $Pb(C_6H_{11}O_7)_2$

Although the properties of lead galactonate are not recorded in the literature, it is easily prepared and should find value for separating galactonic acid for analytical or for preparatory purposes. It may be obtained by neutralizing galactonic acid with lead carbonate or by treating calcium galactonate with lead nitrate. About 15 g of calcium galactonate is dissolved in 100 ml of hot water, and 15 g of lead nitrate added; after cooling to 0° C, about 15 g of crystalline lead galactonate separates. After recrystallization from water and air-drying, the product corresponds to the formula, $Pb(C_6H_{11}O_7)_2$. Analysis calculated for $Pb(C_6H_{11}O_7)_2$: Pb, 34.69. *Found:* Pb, 34.78.

The salt resembles lead gluconate in that it reacts definitely acid and on treatment with slightly more than one equivalent of barium hydroxide gives a basic lead galactonate. The freshly precipitated basic lead salt is so fine that it is difficult to separate by filtration. For analysis the product was separated by centrifuging, washed with water, and dried at 60° C in vacuo. Analysis calculated for $Pb(C_6H_{11}O_7)_2.3PbO.H_2O$: Pb, 64.50. *Found:* Pb, 64.73. The salt contains less lead than the salt,[12] $Pb(C_6H_{11}O_7)_2.4PbO$, obtained by precipitation of galactonic acid with basic lead acetate.

7. LEAD ARABONATE, $Pb(C_5H_9O_6)_2$

Lead arabonate is difficultly soluble and easily prepared either from arabonic acid or from calcium arabonate. Analysis calculated for $Pb(C_5H_9O_7)_2$: Pb, 38.56. *Found:* Pb, 38.59. The new salt exhibits the acidic properties mentioned for the other lead aldonates and in slightly alkaline solution gives a difficultly soluble basic salt which has not been analyzed.

8. LEAD MANNONATE, $Pb(C_6H_{11}O_7)_2$

Lead mannonate was obtained by treating calcium mannonate with an equivalent quantity of oxalic acid, neutralizing the acid set free with lead carbonate, and letting the filtered solution evaporate spontaneously. It separates in slender crystals which frequently

[12] Beilstein's Handbuch der Organischen Chemie, Aufl. 4, 3, 191.

appear needlelike. The air-dried sample contains 34.69 percent of lead which corresponds to the formula, $Pb(C_6H_{11}O_7)_2$. The new salt exhibits the acidic properties noted for lead gluconate and in slightly alkaline solution gives a difficultly soluble basic salt.

9. CALCIUM XYLONATE, $Ca(C_5H_9O_6)_2.2H_2O$

After many attempts during the past 5 years crystalline calcium xylonate was finally obtained from an aqueous solution of calcium xylonate prepared from xylonic γ-lactone and calcium carbonate. The crystals grow slowly in impure solutions but readily when pure. Previously Nef [13] reported that the product he obtained by precipitation of crude calcium xylonate with alcohol was crystalline, but he did not describe it in sufficient detail for the writer to identify it with the above-described product. The crystals, which are slender and pointed like dagger blades, may be separated by filtration and readily purified. When seed is available the substance can be prepared from basic calcium xylonate, or from the product resulting from the electrolytic oxidation of xylose, as described by Isbell and Frush.[14] For analysis the salt was recrystallized from hot water, collected on a filter, washed with aqueous alcohol, and dried in air at room temperature. Analysis calculated for $Ca(C_5H_9O_6)_2.2H_2O$: C, 29.54; H, 5.46; Ca, 9.86. *Found:* C, 29.71; H, 5.47; Ca, 9.92. At 20° C 27.7 g of the salt dissolves in 100 g of water. The specific rotation varies slightly with concentration in aqueous solutions containing less than 5 g per 100 ml. $[\alpha]_D^{20} = +13.5 - .53c$, where c is the number of grams of the salt in 100 ml.

10. CALCIUM α-GLUCOHEPTONATE, $Ca(C_7H_{13}O_8)_2.3H_2O$

Calcium α-glucoheptonate was obtained in the crystalline state, probably for the first time. The first crystals were prepared by evaporating an aqueous solution of calcium α-glucoheptonate obtained from α-glucoheptonic lactone and calcium carbonate. It can be recrystallized from water, but on account of its high solubility (60 g in 100 g of water at 20° C) warm aqueous alcohol is preferable. At room temperature it separates in needlelike crystals which are not suitable for its purification, but at higher temperatures wider and thicker crystals are obtained which can be separated readily from the mother liquor. The product used for analysis was recrystallized from aqueous alcohol at about 50° C and dried at room temperature in air. Analysis calculated for $Ca(C_7H_{13}O_8)_2.3H_2O$: C, 30.86; H, 5.93; Ca, 7.36. *Found:* C, 30.93; H, 5.95; Ca, 7.48. On drying at 100° C in vacuo the loss in weight was 9.96 percent; the sample darkened slightly. In 2.7-percent aqueous solution the hydrated salt gives $[\alpha]_D^{20} = +5.95$.

WASHINGTON, January 22, 1935.

[13] Liebigs Ann. Chem. **403**, 252 (1914).
[14] BS J. Research **6**, 1145 (1931) RP328; and **14**, 359 (1935) RP773.

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EXPERIMENTS ON EXTERIOR WATERPROOFING MATERIALS FOR MASONRY

By Daniel W. Kessler

ABSTRACT

This investigation was concerned mainly with the effectiveness and durability of various types of waterproofings. Thirty-two samples of the more widely used commercial products and ten nonproprietary materials were studied. It is believed that practically all types were represented. Waterproofing effectiveness was rated by the ability of the treatments to reduce the absorption rate of masonry materials. Durability values were obtained by exposing treated specimens to the weather for various periods up to thirteen years. The preservative value of the treatments was studied incidentally.

Wax types were found to be the most durable, but showed the undesirable property of producing discolorations on most masonry materials. The insoluble soaps produced no appreciable discolorations but were not very durable. Fairly satisfactory durability was indicated for the thinned fatty oils and better lasting qualities were obtained for thinned fatty oils with a high melting point paraffin in solution. However, with such types it seems necessary to adapt the consistency of the treatments to the pore structure of the masonry. Treatments which produced a film on the surface, such as normal varnishes of thin consistency, lacquers, and wax emulsions, were not found to be very satisfactory. Treatments consisting of two reacting solutions which produce insoluble precipitates and also treatments which are intended to react with the masonry, were not found to be very effective.

Although the results of studies on preservative value were not sufficient in scope to be conclusive, some evidence was obtained that effective waterproofing materials retard the deterioration of masonry due to the more common weathering actions.

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I. INTRODUCTION

A series of tests to determine the effectiveness and durability of waterproofing treatments on limestone and sandstone was started in 1921. A report [1] was published in 1924 giving the results obtained during a two-year exposure period. The study has since been extended to a larger variety of treatments and a more representative range of masonry materials. Since there is a decided demand for information on the preservative value of masonry treatments, some further experiments were made to determine whether the treatments have merit in protecting masonry from common weathering agencies and from decay due to crystallization of water-soluble salts in the pores.

In addition to twenty-nine proprietary treatments, various non-proprietary treatments and a few purely experimental processes were included in the studies.

The assistance of H. H. Dutton, H. E. Newcomer, and W. H. Sligh in making several thousand determinations of absorption rates is gratefully acknowledged.

II. MATERIALS AND PROCESSES

1. WATERPROOFING MATERIALS

(a) PROPRIETARY TREATMENTS

Samples of the proprietary treatments were supplied by the producers at the Bureau's request. In some cases two or more samples under the same trade name were obtained at different times, which afforded a means of determining variations in composition of the products. The trade names of the proprietary treatments were as follows:

Aquabar
Aquabar no. 2
Aquapel
Anhydrosol
Aridol
Cresolac
Dehydratine no. 2
Dehydratine no. 22
Dehydratine no. 222
Gar-Kem
G. F. no. 100
G. F. no. 145
Glidden's Colorless Waterproofing
Hydrolox
Kemisol
Lastaseal
Lithol
Minwax Clear
N. W. Colorless Waterproofing
Pecora Colorless Waterproofing
Porseal
Protone
Pyramid
Reduced 1017
Seal-A-Pore
Toxloxpore
Transparent Driwal
Tremco
Whigheldt's Xterior Waterproofing

The approximate compositions of these treatments are given in table 1. Where two samples are designated by the same numeral followed by letters, as 1a and 1b, they are two samples of the same trade designation. In some cases the compositions of two samples

[1] Kessler, Tech. Pap. BS **18**, 1 (1924–1925) T248.

of the same trade designation were such as to necessitate their being put under different classifications. Examples of this are as follows: Sample 2 was received under the same trade name as sample 8, sample 11 the same as sample 27, and sample 4 the same as sample 12.

TABLE 1.—*Proprietary preparations*

[Classification and composition]

Designation	Waterproofing ingredients		Volatile thinner, solvent or suspension medium
	Percent	Nature	
THINNED FATTY OILS			
1a	18	China wood oil	Mineral spirits.
1b	27	do	Do.
2	10	do	Do.
3	16	Fatty oil	Petroleum distillate.
4	29	Fatty oil and aluminum soap	Coal tar distillate.
5	10	do	Turpentine and petroleum distillate.
THINNED FATTY OILS AND PARAFFIN			
6a	33	Fatty oil and paraffin (ratio 52:48)	Mineral spirits.
6b	33	China wood oil and paraffin (ratio 43:57)	Petroleum distillate.
7a	38	Fatty oil and paraffin	Do.
7b	26	Fatty oil and paraffin (ratio 83:16)	Do.
8	24	China wood oil and paraffin (ratio 64:35)	Mineral spirits.
THINNED VARNISHES			
9	32	Oils and resins	Mineral spirits.
10	38	do	Do.
11	39	do	Do.
12	38	Coal tar resin	Coal tar naphtha.
ALUMINUM SOAP SOLUTIONS			
13a	4	Aluminum soap	Mineral spirits.
13b	4	do	Mineral spirits and turpentine.
14	3.4	Aluminum soap and wax (ratio 8:1)	Mineral spirits.
15a	7	Fatty oil, aluminum soap, and resin	Petroleum distillate.
15b	12	Heavy mineral oil and aluminum soap	Do.
16	2	Aluminum soap	Do.
17	4.5	do	Petroleum distillate and ethyl acetate.
18	5	do	Coal tar distillate.
19a	4.7	Aluminum soap, fatty oil, and resin	Turpentine and petroleum distillate.
20	?	Aluminum soap and paraffin	Petroleum distillate.
AQUEOUS EMULSIONS			
21a	5	Casein glue and aluminum soap	Water.
21b	3.2	Glue, aluminum soap, and wax	Do.
22	4	Glue and aluminum soap	Sodium soap solution.
23	12	Linseed oil	Sodium carbonate solution.
24	33	Paraffin	Sodium soap solution.
WAX SOLUTIONS			
25a	14	Paraffin	Petroleum distillate.
25b	12	Paraffin and other waxy material	Do.
26a	7	Paraffin	Mineral spirits.
26b	15	do	Do.
27	7	Paraffin and other waxy material	Coal tar distillate.

TABLE 1.—*Proprietary preparations*—Continued

MISCELLANEOUS

Designation	Waterproofing ingredients		Volatile thinner, solvent or suspension medium
	Percent	Nature	
28a	7.5	Cellulose nitrate	Ethyl acetate and acetone.
28b	10	do	Amyl acetate and fusel oil.
29	8.5	Fatty matter and ammonium soap	Diethylene glocol.
30		Fatty oil (about 4 percent) and a high boiling petroleum distillate.	Some lower boiling petroleum distillate.
31	1	Petroleum grease	Petroleum distillate.
32	15	Magnesium fluosilicate	Water.

(b) NONPROPRIETARY TREATMENTS

Ten nonproprietary treatments were tried, but several of these did not give sufficient indications of merit in the preliminary trials to warrant further study. These processes are described in table 2. Process 33 is known as Sylvester's, 34 as Ransome's, and 40 as Caffall's. The others were experimental treatments modeled after those which have been used or suggested as being of possible value.

TABLE 2.—*Nonproprietary preparations*

Designation	Applications	Composition
33	First	2 oz. of alum in 1 gal. of water.
	Second	12 oz. of potassium soap in 1 gal. of water.
34	First	Sodium silicate solution (soda-silica ratio approximately 1:2), density 1.20.
	Second	Calcium chloride solution, density 1.15.
35	Two	Sodium silicate solution (soda-silica ratio approximately 1:2), density 1.20.
36	One	Sodium silicate solution (soda-silica ratio approximately 1:2), density 1.20.
	Followed by several	Limewater.
37	First	10% solution of barium chloride.
	Second	10% solution of aluminum sulphate.
38	One	10% solution of paraffin in gasoline.
39	One	10% solution of beeswax in benzol.
40	One	Paraffin applied with specially designed heating equipment.
41	First	4% solution of ammonium oxalate.
	Second and third	4% solution of calcium chloride.
42	First	10% solution of barium chloride.
	Second and third	10% solution of aluminum sulphate.

2. MASONRY MATERIALS

The greater part of the tests were made on sandstone and limestone of various textures with the expectation that such materials would be representative of the entire range of masonry. During the progress of the studies it was found that masonry materials with different pore structures were not susceptible to waterproofing to the same degree with a given type of treatment; hence a wider range of materials was added, including marble, brick, cast stone, and mortar, with the hope of finding what types of waterproofing were best adapted to various masonry materials. In table 3 the masonry materials are listed with notes on their texture and pore characteristics.

The specimens of natural stone, cast stone, and brick were all cored into cylinders approximately 2⅛ inches in diameter and 2½

inches high. The mortar specimens were cast in the form of cylinders of about the same size as the cored specimens.

TABLE 3.—*Description of masonry materials used in waterproofing tests*

Serial number	Grades and characteristics	Absorption of untreated material 30 minutes
	LIMESTONE	
		Percent
1	Oolitic, grade A	4.49
2	do	3.16
3	do	4.24
4	Oolitic, grade B	4.91
5	do	4.00
6	do	4.12
7	Oolitic, grade C	5.24
8	do	4.48
9	do	5.94
10	Fine grained sandy dolomite	4.50
11	Very fine grained chalky limestone	5.16
12	do	18.35
	SANDSTONE	
13	Medium grained, open pore structure	5.22
14	Fine grained, close pore structure	3.58
15	Coarse grained, open pore structure	6.34
16	Medium grained, open pore structure	4.13
17	Medium grained, close pore structure	3.14
18	Fine grained, open pore structure	6.00
19	Coarse grained, open pore structure	6.50
	MARBLE	
20	Medium grained, saccharoidal texture	0.10
21	Fossiliferous, fine grained matrix	.33
22	Large crystal, calcite	.03
23	Fine grained, calcite	.12
	BRICK	
24	Stiff mud, side cut shale, dense	4.27
25	Dry press, clay, very porous	15.40
26	do	19.09
	CAST STONE	
27	Marble aggregate, pressed, dense	5.04
	MORTAR	
28	1:3 portland cement and building sand	

3. APPLICATION OF WATERPROOFINGS

The proprietary treatments were applied to the specimens with a brush in accordance with the directions supplied by the producers. In most cases this consisted of two applications with an interval of at least 24 hours between coats. The specimens were thoroughly dried before being treated and the waterproofings were applied copiously, that is, until absorption appeared to cease. Since the

specimens were treated under ideal conditions the results may be assumed to represent the maximum waterproofing values that can be attained with such applications.

The nonproprietary treatments were applied as indicated in table 2, except the wax solutions, which were applied like the proprietary treatments. In those treatments consisting of two reacting solutions, as in 33, 34, 37, 41, and 42, the applications were repeated in the order given so the specimens received two or more applications of each solution. Treatment 40 was made by heating the surface of the specimens with a gas flame several degrees above the melting point of the paraffin, after which the molten wax was applied copiously with a brush. The surface of the specimens was then reheated as before.

For each test on a given sample of waterproofing, three specimens of one masonry material were treated.

III. METHODS OF TESTING

The most important characteristics of a waterproofing are the initial effectiveness, E_{w1}, and the rate of deterioration, R_d. The waterproofing effectiveness was measured by the reduction in absorption of the treated material compared to the absorption of the untreated material. For convenience a comparatively short immersion period (30 minutes) was selected. If A_n=the 30-minute absorption before and A_t the 30-minute absorption after treatment, the waterproofing effectiveness, E_w, may be expressed (in percent) as follows:

$$E_w=\frac{(A_n-A_t)100}{A_n}$$

The treated specimens were stored in the laboratory for a few days to dry before the original absorption test was made. Those which showed fairly satisfactory E_w values were exposed to the weather on a roof for durability studies. They were brought into the laboratory at intervals for absorption determinations. A continuous drop in the E_w values during the exposure period indicated deterioration of the waterproofing. The effective period was considered to be the time during which the E_w values remained above 50 percent. The deterioration rate, R_d, may be expressed as the decrease in effectiveness between two determinations divided by the time interval, thus:

$$R_d=\frac{E_{w1}-E_{w2}}{T}$$

where T is the time in years between the determinations E_{w1} and E_{w2}. In determining the R_d values from the effectiveness curves given in figures 1 to 8 where a number of E_w values are available, a straight line, approximating the slope of the E_w curve, was drawn and the intercepts on any two convenient ordinates taken as E_{w1} and E_{w2}. In cases where the E_w curve crossed the abscissa $E_w = 0$ the slope of the line joining this intersection with the initial effectiveness value was used in computing R_d.

IV. RESULTS OF TESTS

1. EXPOSURE TESTS

In figures 1 to 8 the results of exposure tests on 67 series of tests are plotted for exposure periods ranging from one to twelve years. In some cases the tests were continued a few years after the treatments failed to show satisfactory waterproofing values, and in other cases the tests were not continued far enough to show the actual life of the treatments, several being in good condition at the end of twelve years.

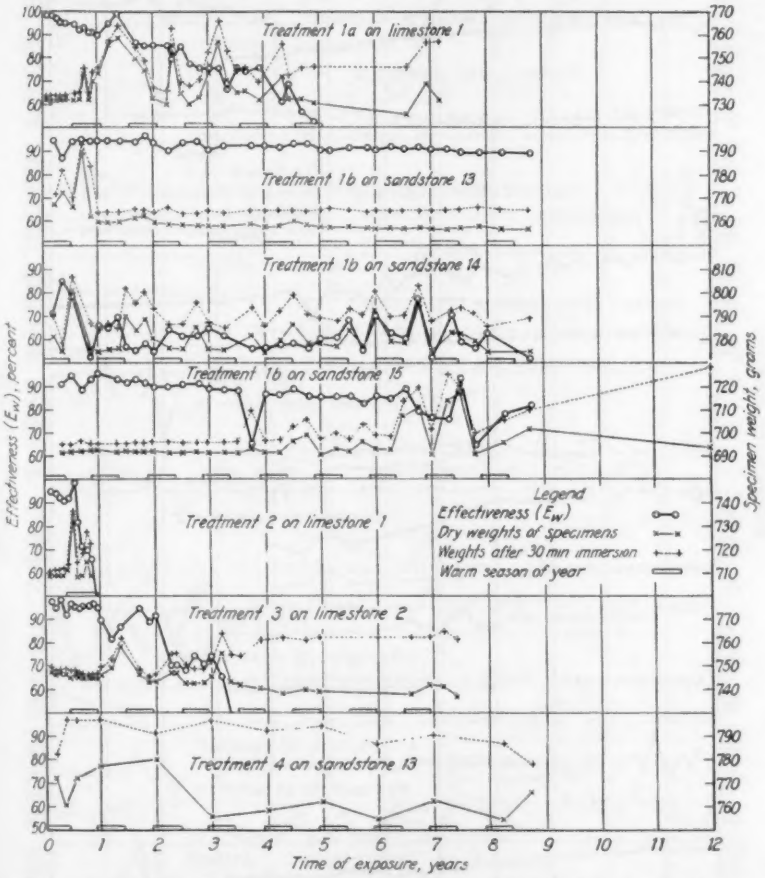
Treatment 1a on limestone 1
Treatment 1b on sandstone 13
Treatment 1b on sandstone 14
Treatment 1b on sandstone 15
Treatment 2 on limestone 1
Treatment 3 on limestone 2
Treatment 4 on sandstone 13
Legend
Effectiveness (E_w)
Dry weights of specimens
Weights after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 1.—*Results of exposure tests on thinned fatty-oil waterproofings.*

A considerable number of tests started from time to time during the progress of the original series were subjected to only occasional absorption tests. These results are not shown graphically but are described briefly. Since in some cases the seasons seem to influence the waterproofing effectiveness, the warm season of the year is indicated by black bars below the curves.

(a) THINNED FATTY OILS

In figure 1 are shown the results of seven series of tests on four proprietary materials of this class. Samples 4 and 5 differ from the others

of this group in that they contain appreciable amounts of aluminum soap. Only one series of tests is shown for preparation 4, but two other series of tests were made with the same on sandstones 14 and 15, which gave results similar to those on sandstone 13. All three were very unsatisfactory. A series of tests with treatment 5 on lime-

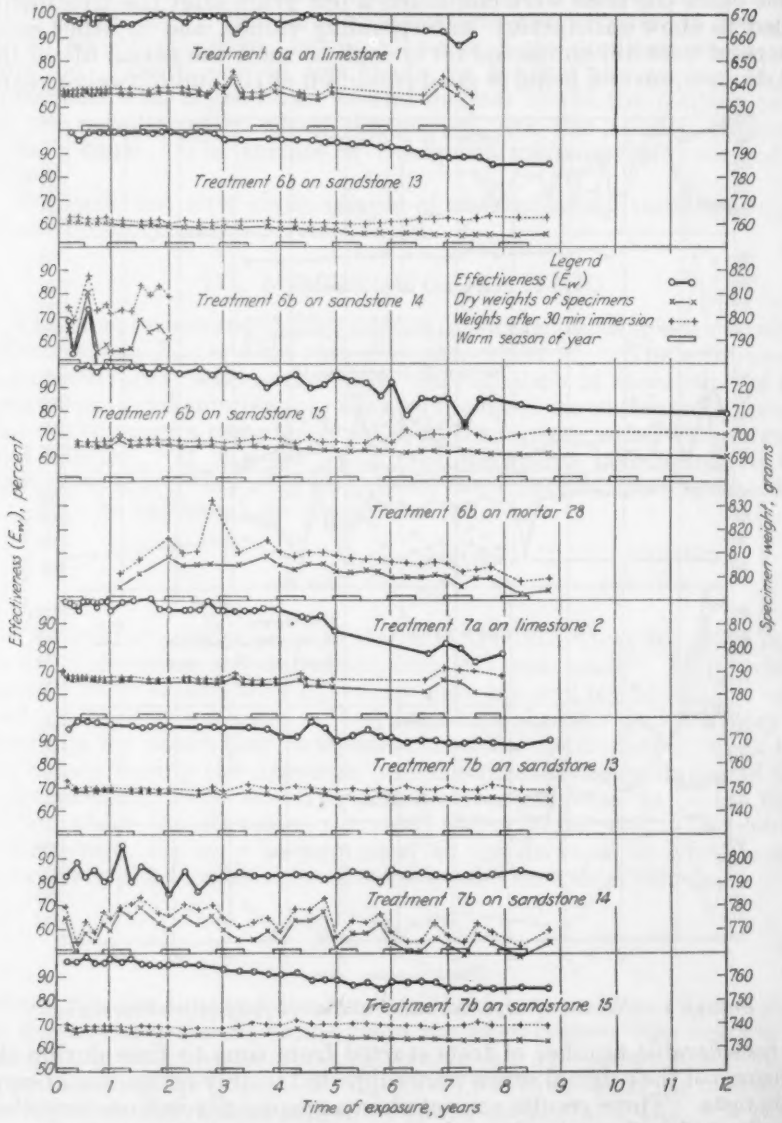
Treatment 6a on limestone 1
Treatment 6b on sandstone 13
Treatment 6b on sandstone 14
Treatment 6b on sandstone 15
Treatment 6b on mortar 28
Treatment 7a on limestone 2
Treatment 7b on sandstone 13
Treatment 7b on sandstone 14
Treatment 7b on sandstone 15
Legend
Effectiveness (E_w)
Dry weights of specimens
Weights after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 2.—*Results of exposure tests on fatty-oil and paraffin solutions.*

stone 5 was continued for four years, but the results are not shown graphically. In this series the results indicated waterproofing values slightly less satisfactory than those shown for treatment 1b on sandstone 13. The higher rate of deterioration of thinned fatty oils on limestone than on sandstone suggests the possibility of saponification

of the oil in contact with limestone. Treatment 1b on sandstone 13 shows high waterproofing values throughout the duration of the tests and indicates that it is well adapted to such pore structures, although not satisfactory on close-pore structures like that of sandstone 14.

(b) THINNED FATTY OILS WITH PARAFFIN

In figures 2 and 3 are shown the results of twelve series of tests with limestone, sandstone, and mortar. This type showed satisfactory

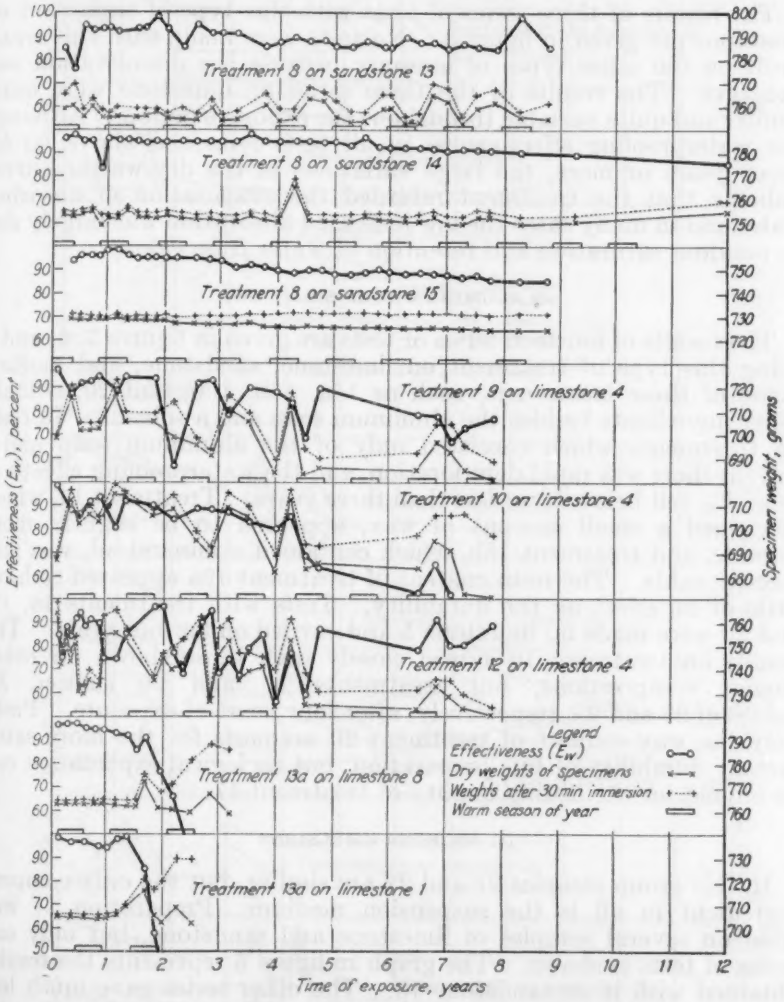
Treatment 8 on sandstone 13
Treatment 8 on sandstone 14
Treatment 8 on sandstone 15
Treatment 9 on limestone 4
Treatment 10 on limestone 4
Treatment 12 on limestone 4
Treatment 13a on limestone 8
Treatment 13a on limestone 1
Legend
Effectiveness (E_w)
Dry weights of specimens
Weights after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 3.—*Results of exposure tests on fatty-oil and paraffin solutions, thin varnishes and aluminum-soap solutions.*

results in all the tests except treatment 6b on sandstone 14. Sandstone 14 in nearly all tests seemed to be particularly difficult to waterproof, but treatment 8 was evidently well adapted to such close-pore structures. Where this type of treatment showed high waterproofing values in the early stages of the exposure tests, the durability

proved to be satisfactory. In the two series carried over a twelve-year period the E_w values were 80 and 85 at the end of the period. The effectiveness curve for the test on mortar is not shown because the original absorption of the mortar was not determined. However, the absorption curves indicate that the treatment was less effective on mortar than on sandstone and limestone.

(c) THINNED VARNISHES

The results of three series of tests with this type of treatment on limestone are given in figure 3. No tests were made with this treatment on the other types of masonry because the discoloration was excessive. The results of the three series on limestone were quite similar and quite variable throughout the exposure period. Although the waterproofing effectiveness in all tests remained above 50 for seven years or more, the large variations in the dry-weight curves indicate that the treatment retarded the evaporation of absorbed water and in many cases the low indicated absorption was largely due to previous saturation and retention of water from rains.

(d) ALUMINUM SOAP SOLUTIONS

The results of fourteen series of tests are given in figures 3, 4, and 5 using this type of treatment on limestone, sandstone, and mortar. Some of these treatments, such as 15a, 15b, 19b, and 20, contain other ingredients besides the aluminum soap and a solvent. In tests on treatments which consisted only of the aluminum soap and a solvent there was rapid deterioration, and the waterproofing effectiveness, E_w, fell below 50 in less than three years. Treatment 14, which contained a small amount of wax, appeared to be slightly more durable, and treatment 15b, which contained a mineral oil, was still more durable. The resin content of treatment 19a appeared to have little or no effect on the durability. Tests with treatments 16, 17, and 20 were made on limestone 5 and carried on for four years. The results on treatment 16 agreed closely with those shown for other similar compositions, but treatments 17 and 20 showed E_w values of 93 and 95, respectively, after four years of exposure. Probably the wax content of treatment 20 accounts for the more satisfactory durability of this preparation, but no logical explanation can be offered for the lasting quality of treatment 17.

(e) AQUEOUS EMULSIONS

In this group samples 21 and 22 are similar, but the only common ingredient in all is the suspension medium. Preparation 21 was tried on several samples of limestone and sandstone, but only one series of tests is shown. The graph in figure 5 represents the results obtained with it on sandstone 13. The other series gave much less satisfactory results. The results obtained on preparation 22 were like those for preparation 21 and are not given graphically. Preparation 23 was tried on limestones 5, 6, and 11, sandstone 17, and marble 22. These tests were carried for four years, but the only satisfactory result in the series was on limestone 6. Treatment 24 was tested on the same materials as treatment 23 and over the four-year period it gave good waterproofing results on all except limestone

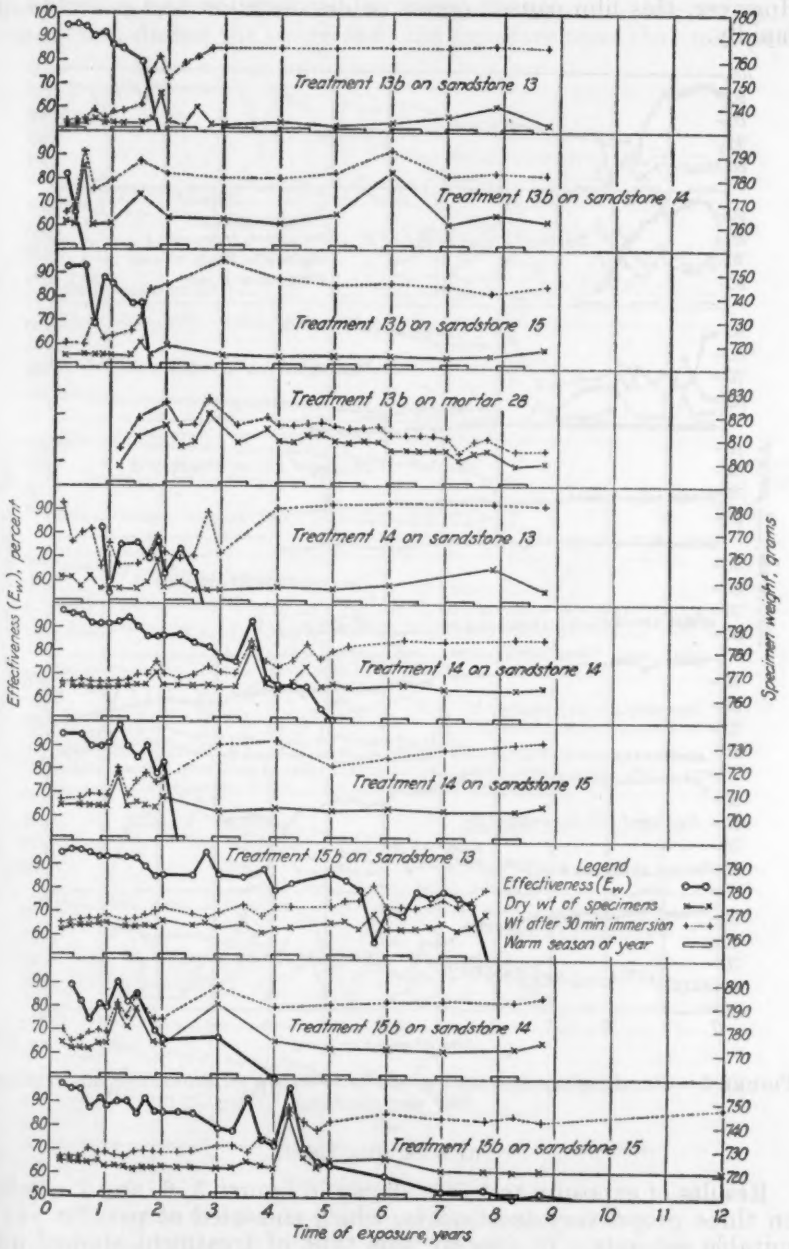
Treatment 13b on sandstone 13
Treatment 13b on sandstone 14
Treatment 13b on sandstone 15
Treatment 13b on mortar 28
Treatment 14 on sandstone 13
Treatment 14 on sandstone 14
Treatment 14 on sandstone 15
Treatment 15b on sandstone 13
Treatment 15b on sandstone 14
Treatment 15b on sandstone 15
Legend
Effectiveness (E_w)
Dry wt of specimens
Wt after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 4.—*Results of exposure tests on aluminum soap solutions.*

10 and marble 22. This appeared to be due to a film of wax deposited on the surface of the specimens, as the penetration was very slight. However, this film caused excessive discoloration and collected dirt rapidly.

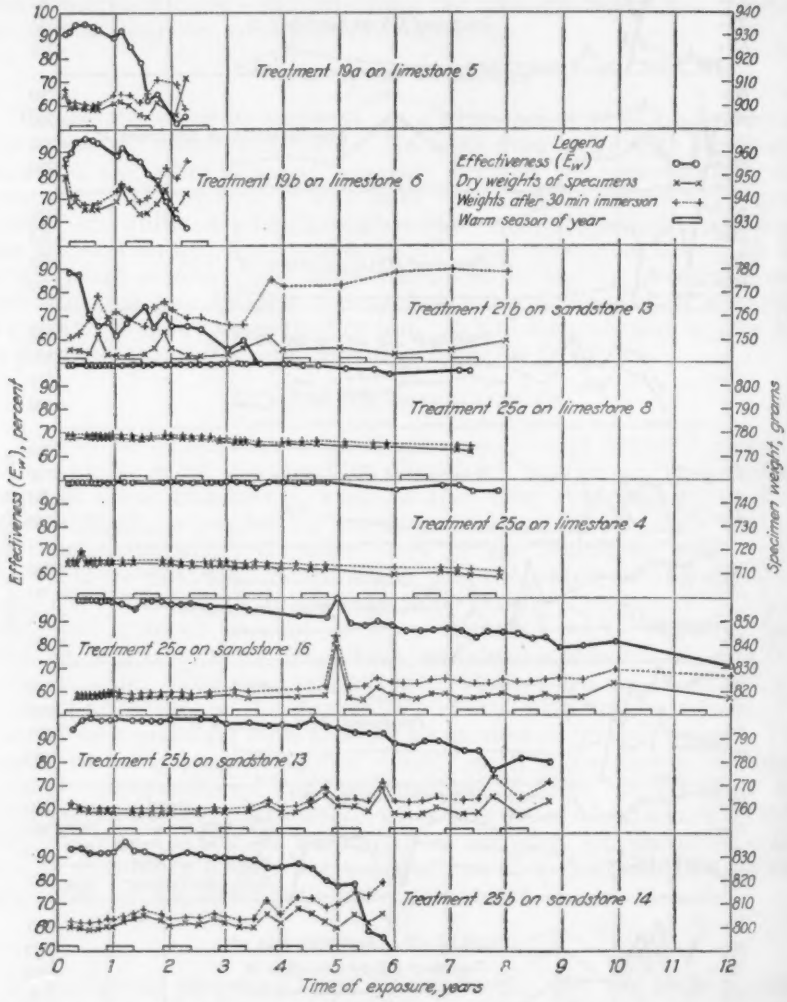
Treatment 19a on limestone 5
Treatment 19b on limestone 6
Treatment 21b on sandstone 13
Treatment 25a on limestone 8
Treatment 25a on limestone 4
Treatment 25a on sandstone 16
Treatment 25b on sandstone 13
Treatment 25b on sandstone 14
Legend
Effectiveness (E_w)
Dry weights of specimens
Weights after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 5.—*Results of exposure tests on aluminum soap solutions, aqueous emulsions, and wax solutions.*

(f) WAX SOLUTIONS

Results of exposure tests are shown in figures 5, 6, and 7 obtained on three proprietary treatments, which consisted of paraffin wax in suitable solvents. In general, this type of treatment showed quite satisfactory durability and high waterproofing values on materials with medium-sized pores. It does not seem to be well adapted to the very fine pore structures, and in some series of tests the results were not very good on the materials with large pores. Possibly a larger

amount of wax in solution would prove more successful on the latter types of masonry. Some of the treatments were still showing good waterproofing values after twelve years of exposure. Occasionally it was found during the progress of the exposure tests that the speci-

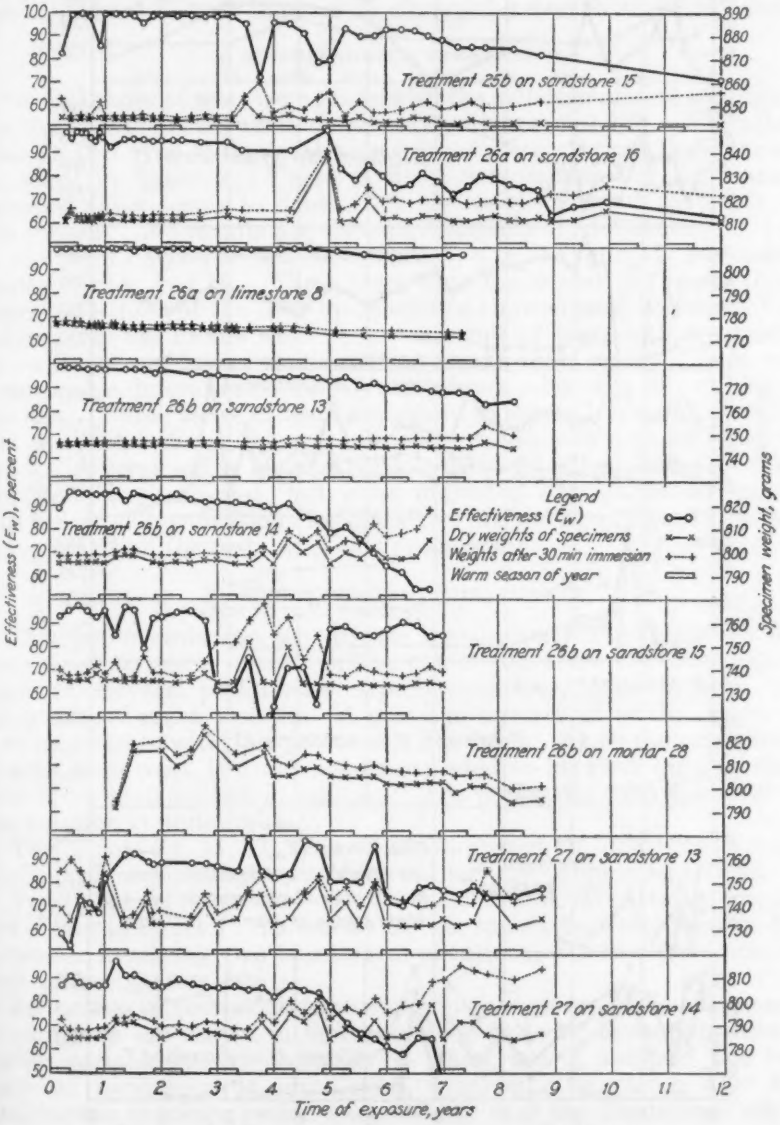
Treatment 25b on sandstone 15
Treatment 26a on sandstone 16
Treatment 26a on limestone 8
Treatment 26b on sandstone 13
Treatment 26b on sandstone 14
Treatment 26b on sandstone 15
Treatment 26b on mortar 28
Treatment 27 on sandstone 13
Treatment 27 on sandstone 14
Legend
Effectiveness (E_w)
Dry weights of specimens
Weights after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 6.—*Results of exposure tests on wax solutions.*

mens had absorbed considerable moisture from rains. This is indicated in the graphs by a sharp rise in the weight curves. Usually these temporary breaks in the waterproofing effectiveness occurred in cold weather. It has been suggested that the wax may crystallize

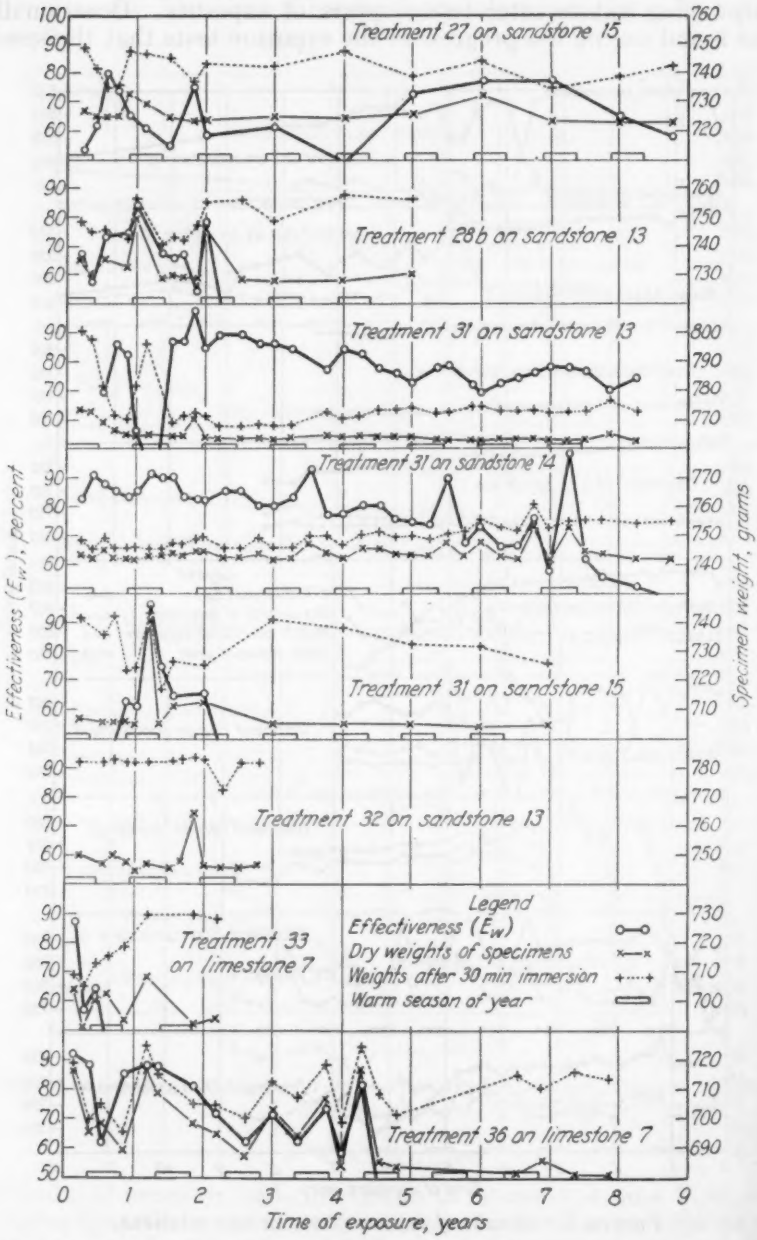
Treatment 27 on sandstone 15
Treatment 28b on sandstone 13
Treatment 31 on sandstone 13
Treatment 31 on sandstone 14
Treatment 31 on sandstone 15
Treatment 32 on sandstone 13
Treatment 33 on limestone 7
Treatment 36 on limestone 7
Legend
Effectiveness (E_w)
Dry weights of specimens
Weights after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 7.—*Results of exposure tests on wax solutions and miscellaneous compositions.*

at low temperatures and in the crystalline form it is not impervious. However, no prominent breaks in effectiveness are shown for the tests on specimens treated by process 40, and some experiments were made on specimens treated by this process by exposing them to low temperatures for several days, then making absorption tests in ice water. There was no increase in absorption due to this procedure.

(g) MISCELLANEOUS TREATMENTS

Several series of tests were made with the cellulose nitrate solutions, but the results are shown in detail only on treatment 28b. The other tests on this type of material were less satisfactory than those shown in detail in figure 7. There is little penetration and the waterproofing value seems to depend mainly on the film which is left on the surface. No results are shown graphically for treatment 29, but it was tried on marble 20, limestones 5, 6, 9, 11, and 12, and sandstones 17, 18, and 19. These tests were continued for nearly three years, and three of the tests on limestone showed good waterproofing values, but the others were poor. A series of tests with treatment 30 on limestone 9 was continued for nearly four years. There was considerable deterioration during this period, with only fair values at the end. Three series of tests are shown in figure 7 on treatment 31, two of which indicate fair waterproofing values over a period of eight years. Several series of tests with treatment 32 on limestone and sandstone were started, but none indicated any particular value. The weight determinations for one series are shown in figure 7, which is typical of all the tests with this preparation.

(h) NONPROPRIETARY TREATMENTS

This group embraces ten diverse treatments. Treatment 33 has been used to some extent and is commonly known as Sylvester's process. Several preliminary experiments were made with it, but none showed much promise. A graph in figure 7 gives the results of a series of tests with this process on limestone. Since the precipitate is aluminum soap, it could not be expected to be more durable than aluminum soap applied in solution. The potassium sulfate formed in the reaction is undesirable.

Treatments 34, 35, 37, 41, and 42 were tried on limestone in some preliminary experiments, but they did not give promising results.

Treatment 36 was tried on limestone 7 and the detailed results are shown in figure 7. It was by far the most effective of any of the processes involving two reacting applications, but the discoloration was quite objectionable.

Five series of tests with process 38 on two grades of limestone and a sandstone are shown in figure 8. The tests on limestone showed rather variable results especially on the grade A stones. The two tests on sandstone 16 gave good waterproofing values over the twelve-year exposure period and indicate that the treatments might continue effective for several more years. Tests were also made with 7, 10, and 14 percent solutions of paraffin (melting point 57° C; 135° F) on bricks 24, 25, and 26 and cast stone 27, which were carried over a five-year exposure period.

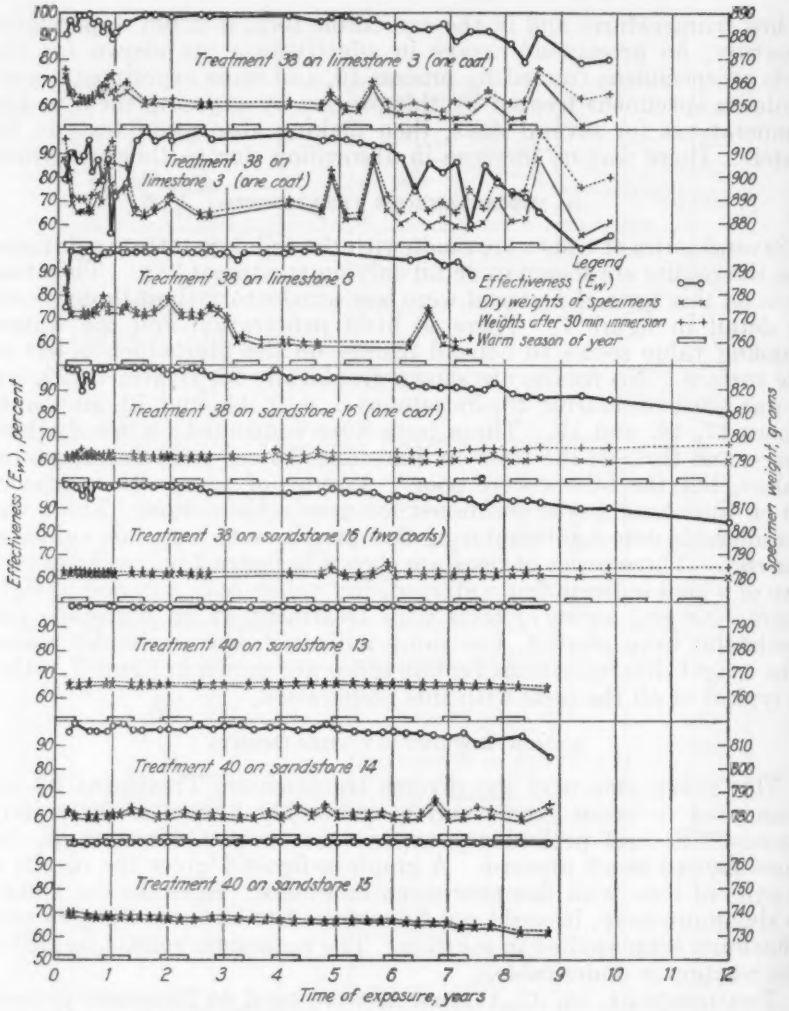
Treatment 38 on limestone 3 (one coat)
Treatment 38 on limestone 3 (one coat)
Treatment 38 on limestone 8
Treatment 38 on sandstone 16 (one coat)
Treatment 38 on sandstone 16 (two coats)
Treatment 40 on sandstone 13
Treatment 40 on sandstone 14
Treatment 40 on sandstone 15
Legend
Effectiveness (E_w)
Dry weights of specimens
Weights after 30 min immersion
Warm season of year
Effectiveness (E_w), percent
Specimen weight, grams
Time of exposure, years

FIGURE 8.—*Results of exposure tests on nonproprietary treatments.*

The E_w values at the end of the period were as follows:

Material treated	Paraffin solution		
	7%	10%	14%
	E_w	E_w	E_w
Brick 24	96	79	72
Brick 25	96	98	98
Brick 26	35	29	15
Cast stone 27	79	82	84

All four of these masonry materials were somewhat like sandstone 14 in having very small pores. The results were quite satisfactory with the 7 percent solution on bricks 24 and 25, with all concentrations very poor on brick 26 and fair on the cast stone. The results were inconclusive as to the effect of solution strengths.

Tests on treatment 39 were carried no further than the preliminary stages because the discoloration was excessive.

Treatment 40 (Caffall process) was tried on three sandstones and carried over an exposure period of nearly nine years. The detailed results in figure 8 show practically no deterioration during this period for the medium and coarse-grained stones. The results were somewhat less satisfactory on the fine-grained stone. The gradual drop in the weight curve for sandstone 15 is believed to be due to the wax flowing out to some extent in hot weather, which indicates the necessity of using a higher-melting-point wax for materials with coarse-pore textures. In all of the tests on this material there was considerable discoloration by dirt collected on the surface. This indicates that it is necessary to remove the excess wax from the surface after treatment.

(i) SUMMARY OF RESULTS

In table 4 the waterproofing samples submitted to exposure tests are listed under the designations given in tables 1 and 2, with the observed initial effectiveness and computed deterioration rates for tests on the types of stone shown in column 2 of table 4.

TABLE 4.—*Initial effectiveness values and deterioration rates*

Waterproofing sample designation	Tested on—		Initial effectiveness (E_{wi})	Deterioration rate (R_d)	Remarks
	Material	Serial number in table 3			
THINNED FATTY OIL COMPOSITIONS					
1a	Limestone	1	99	10	Produced oily discoloration.
1b	Sandstone	13, 14, 15	70 to 95	1 to 4	Do.
2	Limestone	1	97	48	Produced slight discoloration.
3	do	2	98	15	Produced oily discoloration.
4	Sandstone	13, 14, 15	54 to 78	15 to 36	Do.
5	Limestone	6	96	2	Do.
THINNED FATTY OIL AND PARAFFIN COMPOSITIONS					
6a	Limestone	1	99	1	Produced oily discoloration.
6b	Sandstone	13, 14, 15	68 to 99	1 to 2	Do.
7a	Limestone	2	99	3	Do.
7b	Sandstone	13, 14, 15	83 to 97	1 to 2	Do.
8	do	13, 14, 15	86 to 97	1 to 2	Do.
THIN VARNISHES					
9	Limestone	4	98	3	Produced oily discoloration.
10	do	4	99	7	Do.
12	do	4	84	3	Do.
ALUMINUM SOAP SOLUTIONS					
13a	Limestone	1, 8	97 to 99	20 to 26	Very slight discoloration.
13b	Sandstone	13, 14, 15	81 to 95	25 to 60	Do.
14	do	13, 14, 15	20 to 96	9 to 20	Do.
15b	do	13, 14, 15	89 to 97	5 to 10	Do.
16	Limestone	5	80	16	Do.
17	do	5	98	1	Do.
18	Sandstone	19	99	7	Do.
19a	Limestone	5	91	17	Do.
19b	do	6	87	16	Do.
20	do	5	99	1	Slight discoloration.

TABLE 4.—*Initial effectiveness values and deterioration rates*—Continued

Waterproofing sample designation	Tested on— Material	Tested on— Serial number in table 3	Initial effectiveness (E_{si})	Deterioration rate (R_4)	Remarks
		AQUEOUS EMULSIONS			
21a	Limestone	3	67	41	Slight discoloration.
21b	Sandstone	13, 14, 15	44 to 91	11 to 18	Do.
23	do	18	86	18	Produced oily discoloration.
24	Limestone	9	99	5	Produced greasy film.
		WAX SOLUTIONS			
25a	Limestone	4, 8	99	0.4 to 0.5	Produced oily discoloration.
25b	Sandstone	13, 14, 15	82 to 94	2 to 7	Do.
26a	do	16	99	3	Do.
26b	do	13, 14, 15	88 to 98	1 to 6	Do.
27	do	13, 14, 15	52 to 86	2 to 6	Do.
		MISCELLANEOUS COMPOSITIONS			
28a	Limestone	8	79	80	Produced glossy film.
28b	Sandstone	13, 14, 15	69 to 88	14 to 17	Do.
29	do	18	74	8	Produced oily discoloration.
30	Limestone	9	95	8	Do.
31	Sandstone	13, 14, 15	25 to 82	2 to 20	Very slight discoloration.
32	do	13, 14, 15	5 to 43		Do.
		NONPROPRIETARY PROCESSES			
33	Limestone	7	87	62	Very slight discoloration.
36	do	7	92	9	Produced white discoloration.
38	Limestone	3, 8	64 to 91	2 to 5	Produced oily discoloration.
38	Sandstone	16	99	1	Do.
40	do	13, 14, 15	95 to 99	0 to 2	Do.

2. CONTROL TESTS

Two series of tests on untreated specimens were made to determine if the absorption of the stones varied appreciably during exposure. The results are shown in detail in figure 9. Rather wide variations in

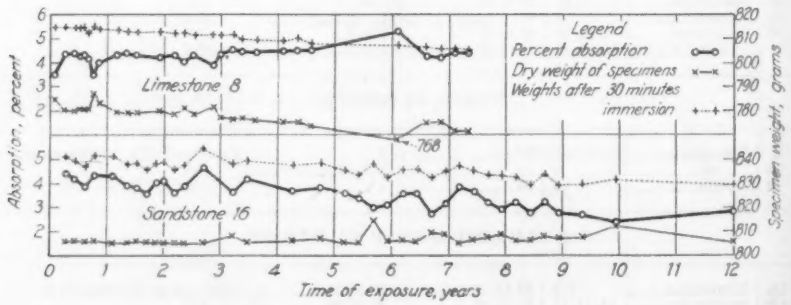

FIGURE 9.—*Exposure tests on untreated specimens.*

the absorption ratio are indicated, but as shown by the weight curves these are, in most cases, caused by the specimens being partly saturated at the first weighing. Another cause of variation was differences in temperature of the specimens and the immersion bath. In winter,

when the specimens were brought in and tested before warming to room temperatures, the absorption values were too low. This was very likely due to expansion of the air in the pores of the specimens when placed in the water bath. This effect was shown very forcefully in a few cases when the treated specimens were immersed cold and partly saturated. In some such cases a negative absorption was indicated which showed that water had been forced out of the pores during immersion. It is also quite possible that the opposite effect came into play to some extent during summer, causing absorption values slightly higher than they normally should be. With a considerable number of determinations it is believed that the average is not far from correct. For the limestone the mean absorption ratio is shown to increase, while for the sandstone it decreased, but in both cases the changes are slight compared with the total absorption. The increase for the limestone is believed to be caused by the enlargement of the pores by the solvent action of rainwater. The decrease for sandstone is probably due to the pores near the surface becoming partly filled with dust.

3. TESTS OF PRESERVATIVE VALUE

Since waterproofing treatments are used occasionally for the purpose of preserving masonry, some studies were also made to determine their effect in reducing the deterioration from weathering. Water plays an important part in most weathering processes and if its penetration into the masonry can be prevented, masonry decay can presumably be reduced. The effects of such treatments in reducing weathering action were studied along the following lines: (1) Solvent action of rain water on calcareous masonry materials, (2) frost action, and (3) decay from crystallization of water-soluble salts.

(a) SOLVENT ACTION OF RAIN WATER

Rain water, being slightly acid, causes by its solvent action a gradual surface roughening of limestone and marbles. However, this surface effect is not of as much concern as the intrapore solution. This action increases the porosity and gradually weakens the bond between the component parts. Calcareous sandstones and other masonry materials consisting largely of inert ingredients cemented together with a matrix that is susceptible to acid action may be more seriously affected by this type of weathering than those that are entirely calcareous.

The rates of solution of a fairly porous limestone and a typical marble for an exposure period of twelve years are shown in figure 10. Both materials were freely exposed to the weather on the roof of a building at the National Bureau of Standards. The weights were determined at each test after thorough drying. The greater rate of solution of the limestone is believed to be due to deeper and more ready penetration of water, thus exposing more surface to the solvent.

All of the waterproofed specimens of limestone and marble showed weight losses during the exposure periods, indicating that even treatments which waterproofed effectively do not prevent surface solution of a calcareous material. Some information on the ability of the waterproofing to prevent intrapore solution may be gained by comparing the weight-loss rate of treated and untreated materials. Such a comparison can be made between limestone 8 in the original condition as

shown in figure 10, and the same material treated with effective waterproofing materials such as treatments 25a and 26a, shown in figures 5 and 6. The weight loss of the untreated stone during seven and one-half years was 1.92 percent. The weight losses for the treated specimens for the same exposure were 0.65 percent in each case.

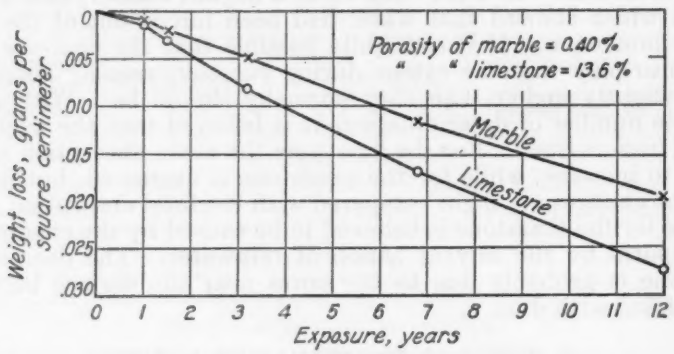

FIGURE 10.—*Solvent action of rain water on marble and limestone.*

Marble 20 (initial absorption 0.10 percent) was treated with seven different waterproofings and exposed to the weather for seven and one-half years for determinations of weathering effect. The percentage weight losses and final absorption of the specimens (each value is the average of three tests) were as follows:

	Waterproofing treatments—						
	1a	6a	13a	m	n	o	p
7½-year weight loss (%)[1]	0.80	0.70	0.92	0.62	0.97	0.72	0.68
Final absorption (%)	.17	.06	.24	.05	.24	.04	.05

[1] Weight loss for a surface area of 129 cm².

Treatments 1a, 6a, and 13a are described in table 1.

The other four were 10-percent solutions of paraffin waxes as follows: m, paraffin (melting point 50° C; 122° F) in gasoline; n, a low-melting-point paraffin in gasoline; o, paraffin (melting point 50° C; 122° F) in solvent naphtha, and p, paraffin (melting point 55° C; 131° F) in gasoline. None of the treatments on this marble gave very satisfactory waterproofing values at the beginning, and it will be noted in three cases the specimens were absorbing more after seven and one-half years than the original marble without treatment. The treatments which lowered the absorption rate appreciably were effective in reducing the solvent action. The loss on the untreated marble was 0.0016 g/cm² per year and for the marble treated with 6a, m, o, and p the average weight loss was 0.007. There were also appreciable differences in the appearance of the specimens, those with more effective treatments being smoother and usually cleaner.

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FIGURE 11.—*Leaching test on limestone panel 1.*
Right-hand half treated with a 10-percent paraffin solution.

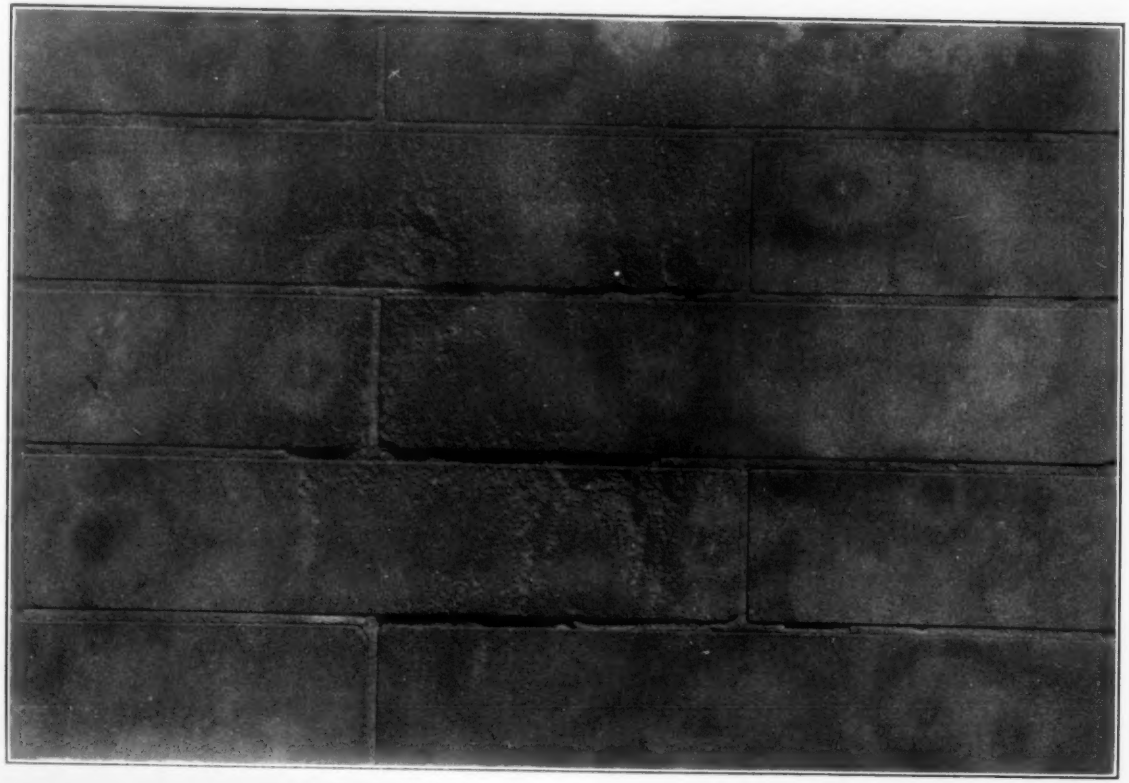

FIGURE 12.—*Leaching test on limestone panel 3.*

Right-hand half treated with a 4-percent solution of aluminum soap.

(b) FROST ACTION

A few tests were made to determine if waterproofing treatments increase the resistance of limestone and sandstone to frost action. The treatment consisted of two coats of a 10-percent solution of high-melting-point paraffin dissolved in benzol. The tests were made under severe conditions, first soaking the treated specimens in water for 14 days and standing them in shallow pans of water while being frozen. They were thawed by immersion in water at about 20° C for 1 hour. Treated and untreated specimens were frozen under the same conditions and the results were as follows:

Material	Number of freezing and thawing cycles causing disintegration of treated and untreated stones			
	No. 15	No. 19	No. 10	No. 6
Treated stone	220	246	187	99
Untreated stone	57	144	95	34

Although these experiments are too meager in scope to warrant final conclusions, they may serve as evidence that an effective waterproofing treatment will increase the frost resistance of such materials. Since the moisture content of masonry walls above grade is usually much less than in the specimens during these experiments, it is safe to assume that the treatment would be more effective in increasing frost resistance under normal service conditions.

(c) DECAY FROM SALT CRYSTALLIZATION

To determine if surface waterproofings are of value in preventing decay from the effects of water-soluble salts crystallizing within the pores of masonry, a series of experiments was made on some panels of limestone-faced brick masonry. Each consisted of a four-inch facing of Indiana limestone backed by four inches of common clay brick, the latter all from a single source.

The entire back face of the brick was coated with a bituminous waterproofing. A coping of the same stone covered the entire top of each panel. Four typical panels are shown in figures 11 to 14. The stone facing is on the south side. The photographs show the present appearance of the facing. The right-hand half of each panel was treated with a waterproofing and the left half was untreated. The mortars used for setting the stone and brick are shown in table 5.

Two blocks of the same limestone as used in the panels were mounted on top of the coping block. Each of these was cored from the top face to give cavities for collecting rain water and causing an excessive amount of leaching through the stone and brick below. This leaching carried to the surface a considerable amount of water-soluble salts existing in the stone, brick, or mortar. After rains the salts were usually conspicuous on the surface of the panels as patches of efflorescence, and the crystallization of the salts within the pores caused more or less spalling or crumbling of the stone.

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TABLE 5.—*Construction of limestone panels* [1]

Panel	Setting mortar		Waterproofing
	Limestone	Brickwork	
1	1 part normal portland cement; 2 parts white sand.	1 part normal portland cement, 2 parts white sand.	All faces of limestone except front and exposed ends painted with bituminous waterproofing material to ½ in. of front face.
2	do	do	None.
3	1 part cement, plus 10 percent lime; 2 parts white sand.	do	Do.
4	do	1 part slag cement, plus 10 percent lime; 2 parts white sand.	Do.
5	do	1 part normal portland cement, 2 parts white sand.	Back of limestone painted with bituminous waterproofing.
6	1 part natural cement; 2 parts white sand.	do	Do.
7	do	1 part natural cement; 2 parts white sand.	None.
8	1 part white portland cement; 2 parts white sand.	1 part normal portland cement; 2 parts white sand.	Do.
9	1 part white portland cement; 2 parts Potomac sand.	1 part white portland cement; 2 parts Potomac sand.	Do.
10	Lime mortar	Lime mortar	Do.
11	Duplicate of panel 1 with C grade limestone.		
12	Duplicate of panel 3 with C grade limestone.		

[1] Panels 1 to 10, inclusive, were faced with grade A limestone similar to limestone 3 in table 3; panels 11 and 12 were faced with grade C similar to limestone 8.

Eleven years have elapsed since the treatments were applied. The individual treatments and notes on the appearance of the stone and mortar are as follows.

Panel 1.—Treated with preparation 38, two coats.

Untreated part.—Noticeable scaling on three stones. The most prominent area of decay covers about four square inches and is one-sixteenth inch deep.

Treated part.—Badly discolored by treatment, but the stone is smooth and shows no decay.

Mortar shows shrinkage cracks along one horizontal joint and is scaling slightly. Treatment did not prevent decay of mortar.

Panel 2.—Treated with two coats of a 15-percent solution of paraffin in gasoline.

Untreated part.—Prominent scaling over one-fourth of surface, one-sixteenth inch deep in several places.

Treated part.—Badly discolored but smooth over most of the surface. About 3 square inches of one block had chipped off, but the appearance is not like that caused by salt crystallization.

Mortar was in good condition over entire surface.

Panel 3.—Treated with preparation 13b, two coats.

Untreated part.—Deep scaling on parts of five stones.

Treated part.—Deep scaling on parts of four stones. The decayed part was near the center of the panel, about two-thirds of the area being on the untreated part.

Mortar crumbled to depth of one-half inch at decayed area of stone and friable over entire panel.

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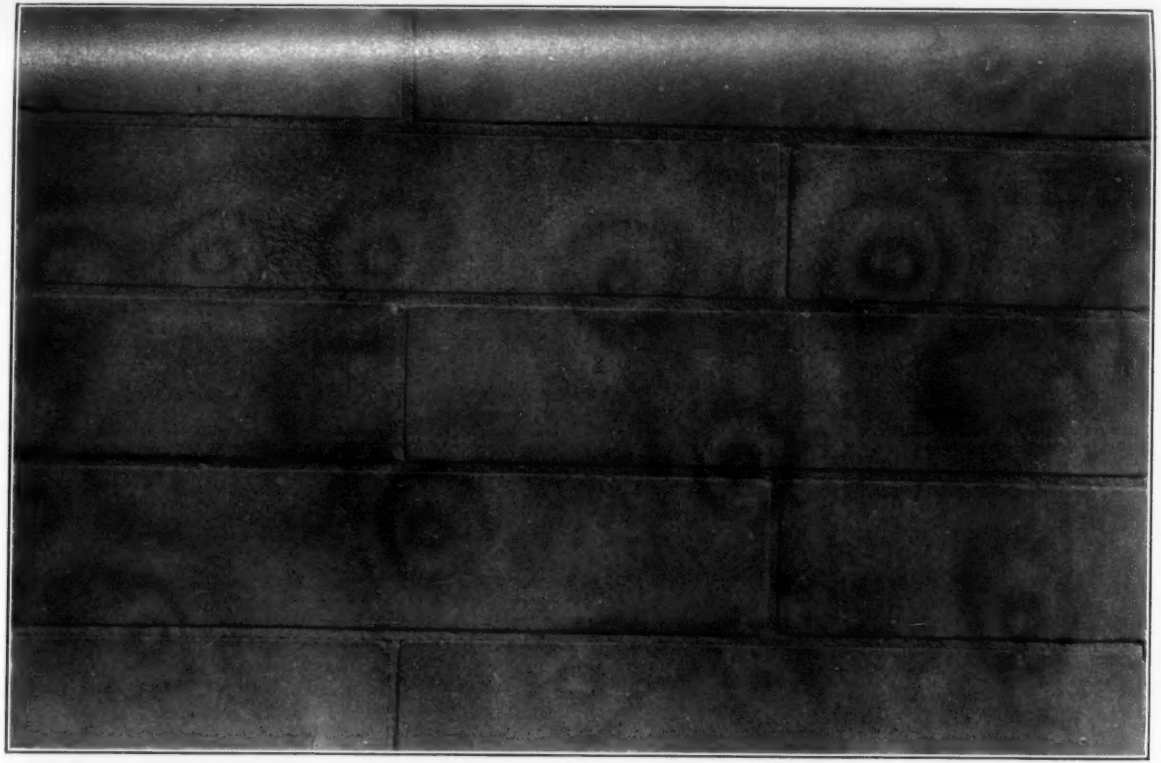

FIGURE 13.—*Leaching test on limestone panel 4.*

Right-hand half treated with a thinned china wood oil.

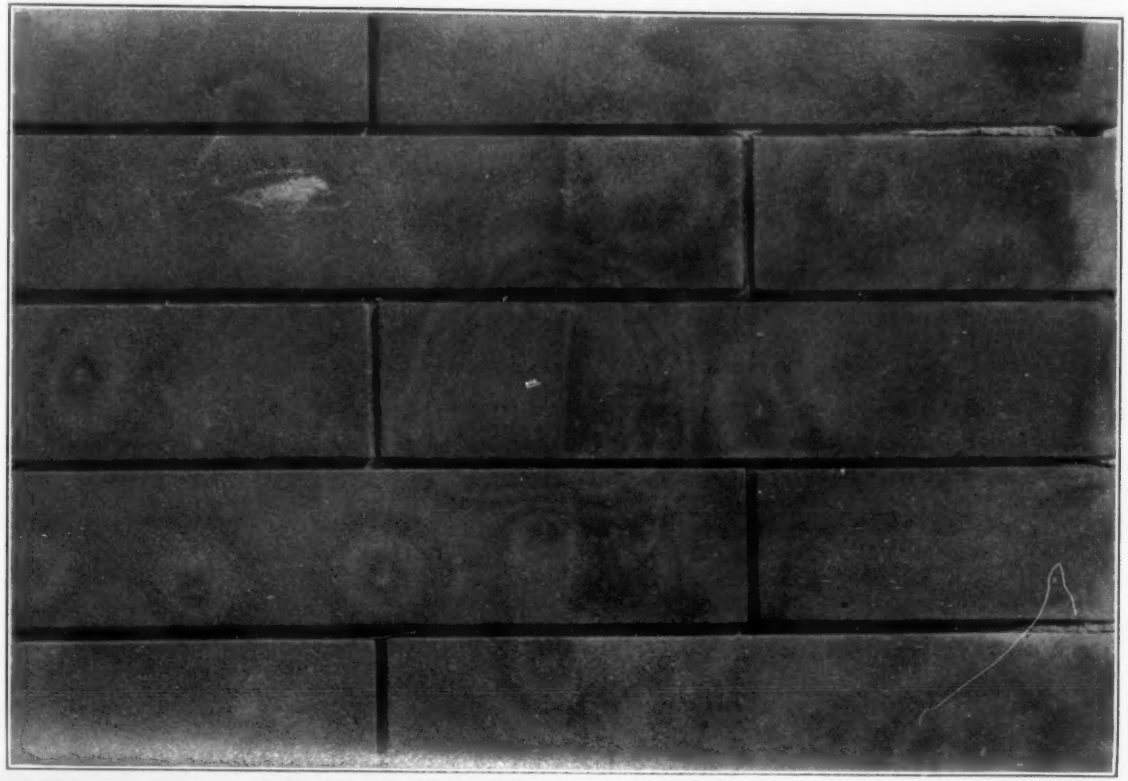

FIGURE 14.—*Leaching test on limestone panel 7.*
Right-hand half treated with a 15-percent paraffin solution.

Panel 4.—Treated with preparation 1b, two coats.
Untreated part.—Small areas of scaling on two blocks, rest in good condition.
Treated part.—Good condition.
Mortar is friable over entire surface of panel.
Panel 5.—Treated with preparation 13b, two coats.
Untreated part.—Prominent areas of scaling on three blocks, rest in good condition.
Treated part.—Similar to untreated part. Decayed area is near center of panel, about two-thirds being on untreated part.
Mortar is friable over entire panel and crumbled to depth of three-fourths inch in some places.
Panel 6.—Treated with preparation 27, two coats.
Untreated part.—Slight scaling on two blocks.
Treated Part.—Good condition and cleaner than untreated part.
Mortar is friable over entire panel but crumbled less on treated part.
Panel 7.—Treated with preparation 26b, two coats.
Untreated part.—Scaling slightly on three blocks.
Treated part.—Stone is discolored considerably, but smooth and in good condition.
Mortar is badly decayed over entire panel and crumbled to depth of one inch in places.
Panel 8.—Treated with preparation 31, two coats.
Untreated part.—Slight scaling on one block.
Treated part.—Good condition and somewhat cleaner than untreated part.
Mortar in good condition over entire panel.
Panel 9.—Treated with preparation 15b, two coats.
Untreated part.—Very slight scaling on one block.
Treated part.—Good condition, but soiled somewhat less than untreated part.
Mortar is sound, but shows a few shrinkage cracks.
Panel 10.—Treated with preparation 19b, two coats.
Untreated part.—Scaling on four blocks.
Treated part.—Slight scaling on one block.
Mortar is crumbling over entire panel.
Panel 11.—Treated with preparation 38, two coats.
Untreated part.—Good condition.
Treated part.—Discolored badly, but in good condition.
Mortar shows shrinkage cracks along all joints and is slightly more friable on treated area.
Panel 12.—Treated with 15 percent paraffin in gasoline, two coats.
Untreated part.—One small area of scaling, but rest is in good condition.
Treated part.—Badly discolored; two small areas spalled, but appearance is not like that caused by salt crystallization.

As noted above, six panels indicated that the waterproofing treatments were effective in preventing decay of the limestone by salt crystallization. The three panels which showed decay from salt action on the treated stone had been treated with a type which has

Right-hand half treated with a 15-percent paraffin solution.

been shown to be effective for only about two years. Two panels treated with a 15 percent solution of paraffin each showed a small area of spalled stone about one inch inside the border between the treated and untreated parts. The appearance of these areas suggests the action of frost rather than salt crystallization. One panel faced with grade C limestone showed no decay on either part. This may possibly be due to the relative capillary properties of the stone and brick. The bituminous waterproofing originally placed on the entire back (exposed) face of the brick did not remain effective for long, but soon scaled off. Hence, it was possible for the moisture which entered the masonry to pass out either through the limestone face or through the brick backing. It seems probable that the moisture was drawn either to the limestone face or to the brick face depending on which material exerted the stronger capillary action.

The bituminous waterproofing applied to the unexposed faces of each limestone block before setting in four of the panels did not show any definite value in preventing decay of the limestone face. Three of these, viz, panels 1, 5, and 6, showed appreciable disintegration of the limestone, but panel 11 did not.

4. DISCOLORATION EFFECTS

The discoloration of masonry surfaces by exterior waterproofing applications was studied by treating half of the face of each slab and comparing it with the untreated portion. There are two considerations in this connection, the initial discoloration and the appearance after weathering. One series of tests made on limestone slabs treated with the various types showed that initially the aluminum soap solutions stained very little, and the thin varnishes most of all. Thinned fatty oils and wax solutions stained in proportion to the amount of wax or oil in the treatment. The molten paraffin process discolored more than the wax solutions, and the cellulose nitrate solution produced a shiny film and splotchy effect. After a few months of weathering most of the discolorations disappeared, and the treated parts of the slabs appeared lighter in color than the untreated parts. After longer exposure there was no appreciable difference between the untreated portions and those with the less durable treatments. However, those with durable treatments remained cleaner for several years.

A similar series of tests was made by applying the treatments on sandstone 13, and marbles 20 and 21. These materials gave a range in color from gray to white, and a range in porosity from 0.5 to 20 percent. The tests indicated that the discoloration by the oil or wax types is greater on the more porous materials. On the very dense and slow-absorbing materials the treatments usually leave a film on the surface. Oil films soon weather away, but a film of paraffin is apt to remain for several years and collect dust.

The limestone panels (described in sec. IV–3–c) which were treated with wax solutions soiled very badly after a few months. This was evidently caused by applying the treatment too profusely, resulting in a film of wax on the surface which held dust particles and caused a soiled appearance. After six or eight years the film started to scale, and caused a mottled appearance.

The lower part of panel 1 was cleaned with an abrasive grit and water. The appearance is shown in figure 11. A moderate amount of scouring served to remove the deposit of dust. An attempt made to clean panel 2 with a wax solvent left a film of about the same appearance as the newly applied treatment.

V. ADAPTABILITY AND SELECTION OF TREATMENTS

As already shown, certain treatments are not equally effective on all types of pore structure. Limestones 10, 11, and 12, sandstone 14, marbles 20, 21, 22, and 23, brick 26, and mortar 28 represent types with finer pore structure that were difficult to waterproof effectively. Oolitic limestones 1, 2, and 3, the finer textures, were not as effectively waterproofed in most of the tests as limestones 4 to 9 with coarser textures. Many tests were made on sandstone 14 with various treatments and in most cases the results were much less satisfactory than the same treatments on sandstone 13, which had a relatively open-pore structure. However, treatments 8 and 14 gave somewhat better results on sandstone 14. Some experiments with 10 percent paraffin and 5 percent China wood oil in high-flash naphtha, applied to various materials of fine-pore structure like sandstone 14, indicated that this composition was well adapted to the type of pore structure that is difficult to waterproof with most of the present proprietary treatments.

It may be expected that treatments having low amounts of nonvolatile matter would prove ineffective on very porous masonry because the residue would not fill the pores to a satisfactory depth. Some evidence in support of this is gained by comparing sandstones 14 and 15 treated with preparations 14, 27, and 31, in figures 4, 6, and 7.

Occasionally manufacturers recommend certain products for use on stone, others for use on brick, and still others for use on concrete. Such designations are not well enough defined since any one class of masonry may have a wide range of pore structure, and waterproofings should be adapted to pore structure rather than to types of masonry. It seems best to determine a suitable treatment for any particular masonry by preliminary experiments with samples of the masonry.

In such preliminary experiments the main points to be determined are waterproofing effectiveness, penetration, and discoloration effects. Rough, dry fragments of the masonry two or three inches in diameter may be treated with the trial composition, and after a drying period of two days subjected to absorption tests of thirty minutes to determine the waterproofing effectiveness. One of the treated fragments broken open and dipped in water will show the approximate penetration of the treatment. Discoloration can be judged by comparing the treated and untreated material. One coat of the waterproofing should reduce the thirty-minute absorption at least 90 percent. Depth of penetration will vary according to the pore structure. For common types of brick, limestone, and sandstone this should be from one-eighth to one-fourth inch, but for denser materials, one-sixteenth inch should prove satisfactory. In cases where no appreciable discoloration is permitted the choice is limited to the stearate type. Since this type is not very durable a compromise between

discoloration and durability may be desirable. The addition of paraffin wax (55° C melting point) to the stearate solution increases both durability and discoloration in proportion to the amount of paraffin added. Where durability is the first consideration and cost secondary, the Caffall process may be chosen. However, there is probably a limit to the size of pores that will successfully retain paraffin at high temperatures even though a high-melting-point wax is used. In some of the tests the wax flowed out and the specimens soon turned black with dirt accumulations. An economical treatment that is very durable may be made by dissolving from six to twelve ounces of a high-melting-point paraffin to the gallon of solvent, such as mineral spirits, naphtha, gasoline, etc. This usually gives high waterproofing values on materials of medium to coarse textures. For fine-pore structures it will be desirable to add from three to six ounces of China wood oil to the gallon of gasoline.

All of the solutions should be applied only when the masonry is dry, and in warm weather. Exponents of the Caffall process claim satisfactory results can be obtained with it on damp walls because the preliminary heating drives the moisture back from the surface. No experiments were made to determine the truth of that claim. Weather temperature with this treatment is evidently not an important consideration.

VI. CONCLUSIONS

The exterior waterproofings of the compositions studied show quite varied effectiveness and durability values. By proper selection of the treatment for any particular masonry it seems possible to obtain good waterproofing results, durability, and some measure of preservative value.

The study has indicated that some compositions may give good waterproofing values when applied to masonry of certain pore structures but inferior results for other types of pore structure. The problem of adapting the waterproofing to the masonry seems to be one of securing adequate penetration. Usually the more viscous solutions and particularly the emulsions do not penetrate to a sufficient depth when applied to masonry having small pores. Specific conclusions relating to the merits of the various types are as follows:

1. The thinned fatty-oil type of treatment appears to be fairly satisfactory on materials of medium texture but not well adapted to the fine-grained or coarse types of masonry. There is probably a slow rate of saponification in contact with calcareous materials. On sandstones of the variety which are satisfactorily waterproofed by this type of treatment, the rate of deterioration is low. Discolorations of an oily appearance are produced by this type.

2. Treatments consisting of fatty oils and paraffin in volatile solvents gave high waterproofing values and satisfactory durability in most of the tests. Those treatments with higher amounts of oil gave less satisfactory waterproofing values on materials of fine pore structure. Discolorations were about the same as for the thinned fatty oils.

3. Thin varnishes did not prove to be very effective and showed a tendency to prevent the escape of absorbed water. The discolorations were more pronounced than for the thinned fatty oils.

4. Aluminum soap solutions usually gave satisfactory initial waterproofing but showed a high rate of deterioration. The discolorations produced by this type were very slight.

5. Aqueous emulsions of waxes and oils gave unsatisfactory results in most of the tests. There seems to be an unsatisfactory penetration of such treatments when applied to most types of masonry, and the film of wax and oils remaining on the surface not only discolors but collects dirt.

6. Paraffin wax dissolved in volatile solvents proved to be very effective and durable on the materials to which the treatment is adapted. For use on fine-pore structures the effectiveness may be improved by small additions of fatty oil. The melting point of the wax should be sufficiently above summer wall temperatures to prevent the flow of wax out of the masonry. For most localities a melting point of 57° C (135° F) is satisfactory. Discolorations of an oily appearance are produced by the treatment.

7. Molten paraffin applied to masonry materials which have been heated somewhat above the melting point of the wax gave very high waterproofing values and had excellent durability. The melting point of the wax should be 57° C (135° F) or higher. Usually a film of wax remains on the surface and should be removed to prevent excessive discoloration and accumulation of dirt.

8. Applications consisting of two separate aqueous solutions that react to produce insoluble precipitates in most cases gave poor waterproofing values and in some cases showed a tendency to cause disintegration.

9. Treatments of the pyroxylin type showed little penetration and the film produced on the surface soon weathered away. This type produces a somewhat glossy and splotchy appearance.

10. The magnesium fluosilicate treatment gave no indications of waterproofing value in any of the tests.

11. Effective waterproofing treatments were of value in increasing the resistance of limestone to frost action, in reducing the destructive effects accompanying efflorescence, and in reducing the solvent action of rain water on calcareous materials.

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AN ACCURATE EBULLIOSCOPIC METHOD FOR DETERMINING THE MOLECULAR WEIGHTS OF NONVOLATILE PETROLEUM FRACTIONS [1]

By Beveridge J. Mair [2]

ABSTRACT

Accurate molecular weights are an essential aid to the chemical investigation of the lubricating oil fraction of petroleum. A modified Cottrell boiling-point apparatus in conjunction with a differential thermoelement has been used to obtain precise values for the boiling-point elevation. The behavior of *n*-nonacosane, anthracene, triphenylmethane, and two oil samples in "isooctane", *n*-heptane, and benzene, and of biphenyl in benzene has been studied. The ebullioscopic constants or apparent molecular weights have been shown to be a linear function of the concentration. Accurate molecular weights are not possible if the customary methods of calculation are employed, no matter what the precision with which the boiling-point elevation is determined. Accurate molecular weights may be obtained if the value of the ebullioscopic constant at infinite dilution is first determined by extrapolation from measurements made over a sufficient range of concentrations. Using this infinite dilution value, the apparent molecular weight of the unknown is computed from observations over a range of concentrations and the molecular weight obtained by extrapolation to infinite dilution. Employing this method, the average value found for the molecular weight of triphenylmethane in "isooctane", *n*-heptane, and benzene was 243.4 compared with the theoretical value 244.14 and for biphenyl in benzene 153.7 compared with 154.08.

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[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research associate representing the American Petroleum Institute.

I. INTRODUCTION

An investigation of the chemical nature of the lubricating oil fraction of an Oklahoma petroleum has recently been undertaken at this Bureau. In the course of this investigation it will be necessary to know the empirical formulas of hydrocarbon fractions and of any hydrocarbons which may be isolated. The molecular weights of the hydrocarbons in the lubricating oil fraction are generally considered to lie in the range from 300 to 700. To assign the correct number of carbon atoms to a hydrocarbon of molecular weight 700 requires that the molecular weight be known to within ± 1 percent. The object of this work was therefore to develop a method by which molecular weights can be determined with an accuracy of ± 1 percent.

II. CHOICE OF METHOD

Two methods only need be considered, namely, the cryoscopic and the ebullioscopic, since the vapor pressures of the fractions of interest in this work are too small to permit accurate vapor-density determinations. Most investigators of the molecular weights of nonvolatile petroleum fractions have used the cryoscopic method. Some of these investigators have used freezing-point measurements at one concentration to determine the molecular weight. Others, namely, Wilson and Wylde (1),[3] Steed (2), Gullick (3), Devine (4), Fenske, McCluer, and Cannon (5) have found that the apparent molecular weight is a function of the concentration and have extrapolated to infinite dilution in an attempt to obtain the "true" molecular weight. If an oil shows a change in apparent molecular weight with change in concentration, it is evident that some value must be given preference to the others and an extrapolation to infinite dilution seems logical. Although such an extrapolation apparently gives the correct molecular weight in a few instances (Steed obtained excellent agreement between the infinite dilution value of the molecular weight of a gasoline determined cryoscopically in nitrobenzene and its molecular weight determined by the vapor-density method), there is plenty of evidence to indicate that it does not invariably give the correct result. Gullick (3) has shown that the molecular weights of some lubricating oils determined cryoscopically in nitrobenzene are not obtained correctly by extrapolation to infinite dilution. Among other obviously incorrect results he found that the infinite dilution value of the molecular weight for a spindle oil was greater than that for a cylinder oil. Fenske, McCluer, and Cannon (5) determined the molecular weights of six pure compounds in cyclohexane. The results show that accurate molecular weights are frequently not obtained with the cryoscopic method even with extrapolation to infinite dilution.

There are two theoretical reasons why the cryoscopic method may give incorrect results even when a high degree of precision is used in the determination of the freezing-point lowering. One of these is that some component of the oil may form mixed crystals with the solvent. This is more likely to occur the more closely the chemical nature of the solvent resembles that of the solute. In this case extrapolation to infinite dilution will not give the true molecular weight.

[3] The figures given in parentheses here and elsewhere in the text correspond to the numbered references at the end of this paper.

The other reason is that such large deviations from the ideal freezing-point law may occur, even at very low concentrations, that incorrect results are obtained on extrapolation to infinite dilution. These large deviations from the ideal freezing-point law are more likely to occur the more dissimilar the chemical nature of the oil and solvent. Thus, with the cryoscopic method, if a solvent similar in chemical nature is chosen, mixed crystals may result; with one dissimilar in nature, large deviations from the ideal solution laws are possible. With the ebullioscopic method, the question of mixed crystals does not enter, and a solvent may be chosen which resembles the solute as closely as possible so that deviations from ideality are kept at a minimum.

Another practical consideration favors the boiling-point method. The solubility of hydrocarbon oils and waxes of high molecular weight in many solvents at the freezing point is limited, so that few solvents are available for selection. At the boiling point the solubility is much greater and a much greater number of solvents are available.

The boiling-point method is applicable only to fractions whose boiling points are at least 150° C, and preferably 175° C, higher than the solvent.

Although the ebullioscopic method possesses these theoretical and practical advantages it has been used comparatively little to determine the mean molecular weights of lubricating oils. This is probably because the ebullioscopic method has hitherto been considered less precise than the cryoscopic method. One of the difficulties encountered with the ebullioscopic method, namely, superheating, has been removed by the development of the Cottrell (6) boiler. A further difficulty with boiling-point measurements has been the control of the atmospheric pressure above the boiling liquid or the correction of the boiling-point data to a standard atmospheric pressure. This difficulty has been obviated by Washburn and Read (7), who made simultaneous readings of the boiling points of two Cottrell boilers, one containing solution and the other pure solvent. This difficulty is also obviated in the apparatus of Menzies and Wright (8), in which a differential thermometer in a single Cottrell boiler is used.

Accordingly, the ebullioscopic method was chosen for further investigation and the present paper covers a detailed description of the apparatus and procedure developed, together with preliminary data on the use of three different solvents. The apparatus involves a number of improvements over that employed by the above-named investigators, and evidence is presented that the method is convenient, rapid, and capable of giving an accuracy of 1 percent.

III. DESCRIPTION OF APPARATUS

The apparatus consisted of (a) two vacuum-jacketed Cottrell boilers, one for solvent and one for solution, equipped for electrical heating; (b) a ten-junction differential thermoelement for measuring the boiling-point elevation; and (c) a special thermoelement potentiometer of high accuracy.

1. COTTRELL BOILERS

The Cottrell boilers were designed by M. M. Hicks-Bruun and were similar to those used by Washburn and Read (7) and Pearce and Hicks (9). One of these Cottrell boilers of a heat-resistant

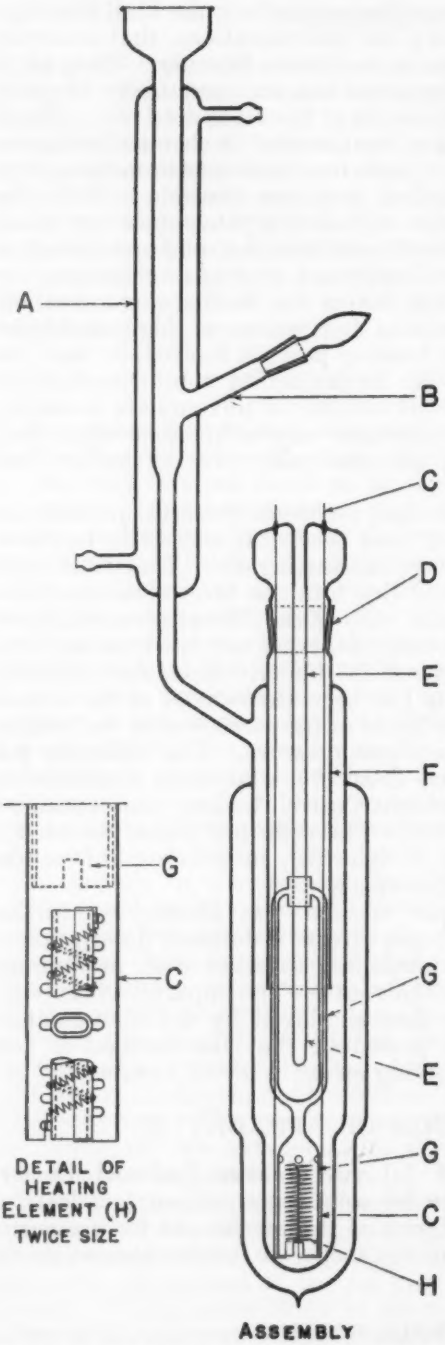

FIGURE 1.—*One of the modified Cottrell boilers*

glass is shown schematically in figure 1. Through the wall of the condenser (A) is sealed a side tube (B), fitted with a ground-glass stopper used for the introduction of liquid solutes. Solid solutes were added through the funnel-shaped top of the condenser. Through the ground-glass stopper (D), heavy tungsten leads (C) were sealed which ran close to the bottom of the apparatus and to which was hard soldered the heating unit (H). The pumping apparatus (G) was held by the tungsten leads and heating unit and was removable with the ground-glass stopper. The thermoelement well (E), the lower portion of which was made of thin glass, was also supported by the ground-glass stopper. The thermoelement wells were filled with a nonvolatile, highly refined mineral oil. (F) is a glass sheath which serves to protect the thermoelement from the influence of cold liquid running from the condenser. When filled to slightly above the pumping bell, the apparatus contained approximately 30 ml of liquid.

2. HEATING UNIT

The heating unit lowered below the bell of the pumping apparatus is shown in detail in the inset of figure 1. The heating unit, made of no. 26 B. & S. gage nichrome wire was first tightly coiled, then wound around a glass frame, inserted in the bell of the pumping apparatus, and hard-soldered to the tungsten leads. The glass frame consisted of a somewhat flattened glass tube to which were sealed glass knobs to prevent contact between the spirals of the heating coil. The upper end of the wire was led out through the glass tube. The

resistances of the heating units for the two boilers were made approximately equal, one being 19.0 and the other 18.9 ohms.

3. POTENTIOMETER

The potentiometer was designed by Brooks and Spinks (10) and constructed especially for use with the ten-junction copper-constantan thermoelement to determine accurately small temperature differences. In the usual instrument the unknown emf is balanced by an equal potential difference, obtained by changing the value of resistance between the two tap-off points on a circuit in which a current is maintained at a preassigned standard value. In this instrument, however, the unknown emf is balanced by an equal potential difference obtained by changing the value of current flowing through standard resistances. This change from the usual design made possible an instrument extraordinarily free from parasitic emf. Provision was also made in the instrument for detecting and eliminating parasitic emf in the galvanometer circuit.

The potentiometer was graduated to read directly in degrees centigrade and not in units of emf. The instrument has six ranges, namely, from 0° to 0.1°, 0.2°, 0.5°, 1°, 2°, and 5° C, respectively, each range subdivided into 100 divisions readable by estimation to 0.1 division. A description of the method of calibration of the potentiometer scale for use with the group of ten copper-constantan couples is given by Brooks and Spinks (10). Since the potentiometer was graduated to read directly in degrees rather than units of emf, provision for compensating for the variation of $\frac{dE}{dT}$ with T was provided. In practice it was necessary only to set a dial (the bath temperature dial) at the boiling temperature of the solvent.

4. THERMOELEMENT

The ten-junction thermoelement was made from no. 30 B. & S. gage constantan wire, tested for homogeneity, and from no. 40 B. & S. gage copper wire. The junctions were soldered, using rosin as a flux, and insulated from each other with bakelite varnish. The thermoelement was calibrated by the heat division of this Bureau. Calibration is not essential, for no error would be introduced into the determination of molecular weights, since the apparatus is calibrated for each solvent with substances of known molecular weight. All that is necessary is that the relation of temperature to emf for the thermoelement remain constant throughout the experiments. The Cottrell boilers were placed close together so that as little as possible of the thermoelement was exposed. The thermoelement extended 22 cm into the wells and the distance between wells was 7 cm.

IV. METHOD AND PROCEDURE

1. CONSTANCY OF HEATING CURRENT

In any determination of molecular weights by the boiling-point method, the question as to what is the composition of the solution in contact with the temperance indicator arises. Solvent is absent from the solution both as vapor and as condensate on the walls of the vessel, and the concentration is not that calculated from the weights

of solvent and solute introduced. The method employed in this instance to get around this difficulty is to supply energy at a constant rate to the apparatus so that the amount of solvent absent from the solution remains constant. The apparatus can then be calibrated for each solvent with substances of known molecular weight.

Direct current from lead storage batteries at 70 v flowed through the Cottrell heaters connected in series with one another and in series with a variable external resistance and an ammeter. The current necessary for steady operation was noted for each solvent and in subsequent work the ammeter was brought to the same reading within ± 0.02 amp. The effect of variation in current on the boiling-point elevation was observed in a few cases. For a solution of 1.3116 g of triphenylmethane in 19.883 g of *n*-heptane, ΔT equalled 1.020° and 1.036° C for currents of 1.35 and 1.55 amp, respectively. If a precision of 0.2 percent is required, it is necessary to keep the current constant within ± 0.025 amp. The currents used were 1.40 amp for benzene and 1.45 amp for *n*-heptane and "isooctane."

2. LOSS OF SOLVENT FROM THE APPARATUS

In order to prevent loss of solvent, the ground-glass stoppers were tightly sealed by flowing a small quantity of lubricant into the upper rim of the ground-glass joint. Tetraethylene glycol citrate resin was used when benzene was the solvent employed. At the temperature of boiling heptane and "isooctane", this substance is rather fluid and ethylene glycol citrate resin was used instead. These resins, obtained from T. P. Sager (11), are insoluble in aromatic and aliphatic hydrocarbons.

3. INFLUENCE OF LIGHT ON THE THERMOELEMENT

The Cottrell units with thermoelement were placed on a table about 2 feet from a window, one unit being closer to the window than the other. Apparently, unequal radiation fell on the two legs of the thermoelement or else their surfaces were not identical and adsorbed radiation in a different manner. The observations reported in table 1, made on a cloudy day with pure benzene in both boilers, show the effect of light.

For this reason the observations were always made with the shades entirely down, and with both Cottrell boilers covered with black cloth.

TABLE 1.—*Data showing the influence of light on the thermoelement*

Cottrell unit with the higher temperature	Time	ΔT	Position of shades	Cottrell unit with the higher temperature	Time	ΔT	Position of shades
A	2:12	0.0005	Down.	B	2:23	.0149	Up.
A	2:15	.0012	Do.	B	2:26	.0155	Do.
B	2:16	.0065	Half-way up.	A	2:27	.0005	Down.
B	2:20	.0060	Do.	A	2:29	.0007	Do.

4. PROCEDURE

A known weight of solvent was introduced into one of the boilers by means of a weighing pipette with a long side arm,[4] inserted several inches into the apparatus to minimize loss by volatilization. Into the other boiler approximately the same quantity (30 ml) was added from a graduated cylinder. The ground-glass stoppers were inserted, lubricant was flowed around their rims, and the thermoelement inserted in its well, the room darkened and boiling started. After about 20 minutes, readings of the temperature difference between the two Cottrell boilers were started. Even with pure solvent in both boilers a difference of temperature occasionally as great as 0.008°, but usually from 0.002° to 0.004° C was observed. The readings of this difference were generally constant to within ±0.0005° C, although sometimes variations amounting to ±0.0010° C were observed. After this difference in temperature had been determined a weighed portion of solute was added. The solid solutes were added in the form of pills. The liquid solutes were added from a weighing pipette with a long side arm, care being taken that all the solute fell into the central condenser tube. The heating current was temporarily increased in order to raise the reflux level and wash all the solute into the lower part of the boiler. The heating current was then returned to its predetermined value, and after about 15 minutes, readings of the temperature difference were begun. About 5 or 6 readings were taken at 2 to 3 minute intervals. These readings, usually constant to within ±0.0005° C, were averaged and corrected for the difference observed when pure solvent was in both boilers.

5. SOLVENTS

Three hydrocarbons, benzene, *n*-heptane, and "isooctane" (2,2,4-trimethylpentane) were used as solvents. These were chosen for variety of type and because they are available commercially in reasonably pure condition. Since each solvent is calibrated, exceptional purity does not seem necessary, provided very volatile constituents are absent. The benzene, which conformed to American Chemical Society specifications for reagent benzene, was distilled once through a very efficient fractionating column and the first and last fifths were rejected. The *n*-heptane used was obtained from the California Chemical Co., and had the following constants: Freezing point −90.7° C, boiling point 98.4° C, $D_4^{20}=0.6837$, $n_D^{20}=1.3878$. The "isooctane", a mixture of commercial samples, had a refractive index $n_D^{25}=1.3890$ and froze over a range of 0.5° C.

6. SOLUTES

The hydrocarbons used as solutes, *n*-nonacosane, anthracene, triphenylmethane, and biphenyl, also were chosen with a view to variety of type and availability. The *n*-nonacosane was a sample of exceptional purity, prepared by Doctor K. S. Markley, Bureau of Plant Industry, U. S. Department of Agriculture, from Rome Beauty apple cuticle. Certain constants for this material obtained by Markley are compared in table 2 with those obtained by Piper, et al. (12) for pure synthetic *n*-nonacosane.

[4] Similar to that shown by Findlay, Practical Physical Chemistry, page 126, Longmans, Green and Co. 1925).

TABLE 2.—*Constants of n-nonacosane*

Constants	Temperatures obtained by—	
	Markley	Piper, et al.
	°C	°C
First transition on heating	57. 5–57. 7	57. 5
Second transition on heating	62. 7	
Melting point	63. 5–63. 7	63. 4–63. 6
Setting point	63. 1–62. 9	63. 2
First transition on cooling	60. 2	
Second transition on cooling	55. 2	56. 0

Doctor Sterling B. Hendricks, Division of Fertilizer Investigation, Bureau of Chemistry and Soils, submitted the above specimen to X-ray examination with the following results: Using a pressed-on-glass specimen and Cr-K radiation, a spacing of $d_{(001)}=39.00\pm.20$ *A* was obtained. (Compare Piper et al., $d_{(001)}=38.68$ with an accuracy of 1 percent.) The original plate showed eleven orders of reflection with little diminution of intensity toward the end of the plate. The dimensions of the plate would not permit the observation of orders beyond the eleventh. Eight or more orders of reflection is one of the criteria of purity listed by Piper et al.

Anthracene from Kahlbaum was purified by the method of Winterstein and Schön (13) who obtained pure anthracene by removing the colored compounds from technical anthracene by adsorbing them on active alumina from a benzene solution. The same method was employed here, both active alumina and silica gel being used. The silica gel seemed quite as effective as the alumina in removing color. The anthracene was then crystallized once from benzene and the solvent removed by heating in vacuum. The anthracene thus obtained melted at 216° C.

Eastman's triphenylmethane (catalog no. 833), melting at 92.0° C, was crystallized once from alcohol. This purified material melted slightly higher, at 92.5° C.

The biphenyl melted at 67° C, compared with 69° C for a sample of Eastman's (catalog no. 721). These melting points were made by the capillary tube method and are not reliable to better than ±1° C.

With the exception of the *n*-nonacosane, which was very pure, no claim is made for exceptional purity for these compounds. The biphenyl was less pure than the others. It was used only in preliminary experiments with benzene as a solvent, since its vapor pressure is sufficiently high at 100° C (4.35 mm) to cause appreciable errors, with the higher boiling solvents.

Two samples of oil from the same Oklahoma crude were investigated. One of these was a "water white" sulphur-free oil obtained by filtration through silica gel; the other a highly colored sulphur dioxide extract. Certain physical characteristics of these oils are recorded in table 3. These samples correspond in physical properties to a "paraffin" base oil and to a "naphthene" base oil.

TABLE 3.—*Certain physical characteristics of oil samples*

Sample	Refractive index n_D^{25}	Density at—		Kinematic viscosity at—	
		150° F	210° F	150° F	210° F
		g/ml	g/ml	*Stokes*	*Stokes*
Silica gel filtrate "water white"	1.4674	0.817	0.794	0.0775	0.0367
Sulphur dioxide extract "highly colored"	1.5485	.976	.951	.2006	.0780

V. EXPERIMENTAL RESULTS

The results of the calibration experiments for the three solvents, using as calibrating solutes *n*-nonacosane and anthracene, are shown in figure 2, in which the ebullioscopic constant $K=\frac{\Delta T}{x_1}$ (where ΔT is the boiling-point elevation and x_1 the mole fraction of solute) is shown as a function of the concentration in mole percent. It is apparent that K is far from being independent of the concentration, and furthermore that K at any finite concentration for any solvent also depends on the chemical nature of the solute. A lineal relationship seems to exist between K for each solute and the concentration. The values for K for the two solutes approach each other at low concentrations. It is seen that the data are reproduced within the experimental error if the lines for the two solutes are extrapolated to give the same value for K at infinite dilution. It is apparent that one method of computing molecular weights, i. e., determination of the constant K for the solvent by the use of a solute of known molecular weight at a finite concentration, and the use of this constant to compute the molecular weight of the unknown from observations at approximately the same concentration may lead to gross errors. This method of computation when used to calculate the molecular weight of anthracene from the constant K for *n*-nonacosane at 1.2 mole percent in heptane, "isooctane", and benzene, gives results higher than the theoretical by 4.8, 4.2, and 1.8 percent, respectively. The only method of calculation, which will lead to the theoretical molecular weight of anthracene, is a computation of the apparent molecular weights of anthracene at various concentrations from the infinite dilution value of K (from *n*-nonacosane), and extrapolating to infinite dilution these apparent molecular weights as a function of concentration. Obviously the molecular weight of *n*-nonacosane may be obtained in a similar manner from the value of K for anthracene at infinite dilution.

The precision attained in these calibration experiments, and the values obtained for K by extrapolating lines through the data for *n*-nonacosane and anthracene to a common point are shown in table 4.

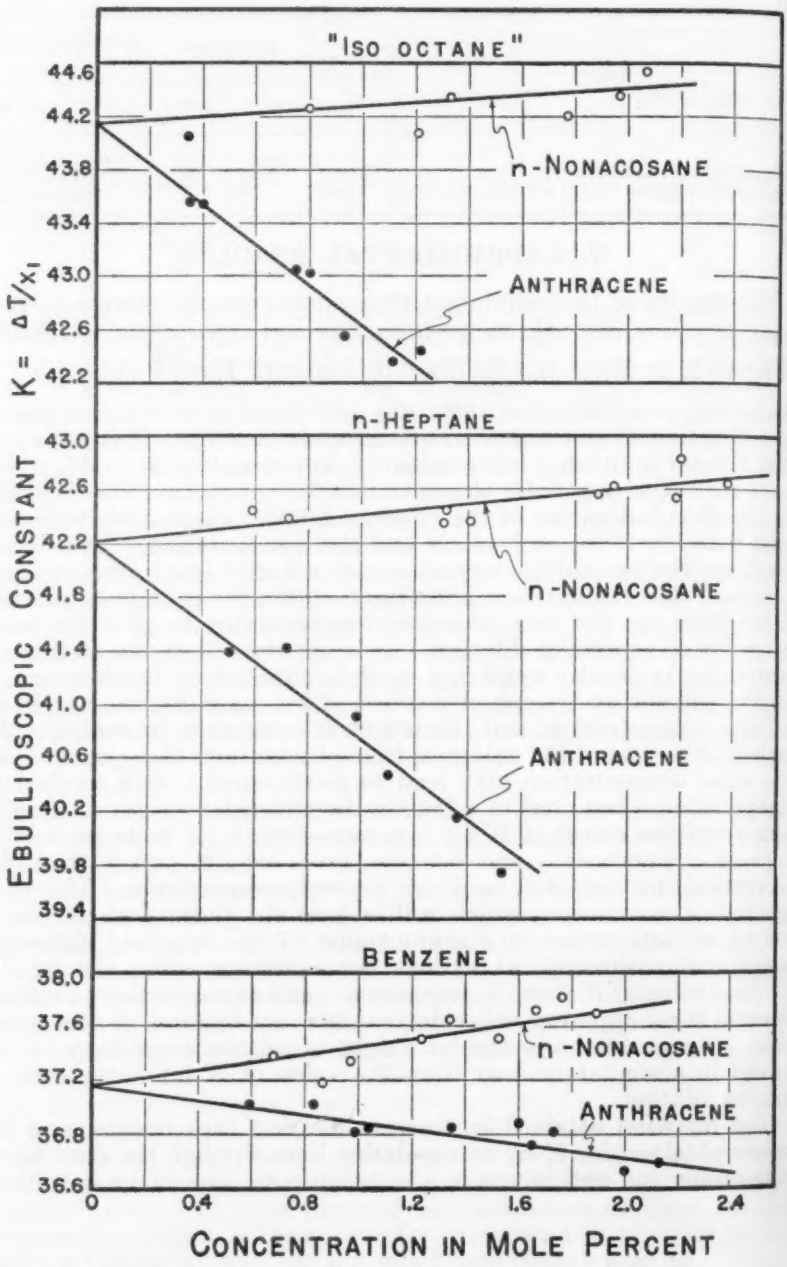

FIGURE 2.—*Ebullioscopic constants* $K=\frac{\Delta T}{x_1}$ *as a function of concentration in mole percent for three solvents, "isooctane", n-heptane, and benzene.*

○ and ● represent values for *n*-nonacosane and anthracene, *respectively.*

TABLE 4.—*Summary of calibration experiments*

Solute	Solvent	Maximum deviation of values from extrapolation line	$K=\frac{\Delta T}{x_1}$ Lim. $x_1=0$
		Percent	
Anthracene	"Isooctane"	one value at low concentration off + 1; all others within ± 0.15.	44.14
n-nonacosane	do	±0.55	
Anthracene	n-heptane	±.65	42.20
n-nonacosane	do	±.45	
Anthracene	Benzene	±.38	37.16
n-nonacosane	do	±.67	

As a further check on the validity of this method of calculation, and on the accuracy with which the infinite dilution values of K for all three solvents had been obtained, experiments with biphenyl in

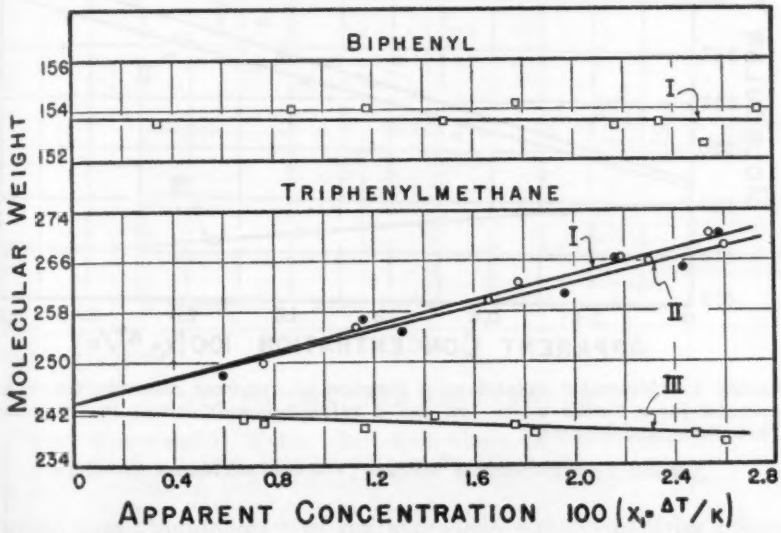

FIGURE 3.—*Molecular weights as a function of apparent concentration in mole percent for biphenyl in benzene and triphenylmethane in "isooctane", n-heptane, and benzene.*

○, ●, and □ represent values in "isooctane", n-heptane and benzene, respectively.

benzene, and triphenylmethane in all three solvents were made. The results of these experiments are shown in figure 3. Biphenyl in benzene shows very little if any change in apparent molecular weight with change in concentration, and the data lead to the value 153.7, in close agreement with the theoretical value 154.08. Triphenylmethane in benzene shows a small decrease in apparent molecular weight with increase in concentration, while in heptane and "isooctane" there are marked increases in apparent molecular weight with increase in concentration. By separate extrapolation to infinite dilution of the values obtained in benzene, "isooctane", and heptane, the values 242.6, 243.6, and 244.1, respectively, are obtained in close agreement with the theoretical value 244.1.

In figure 4 are shown the apparent molecular weights of the two oil samples as functions of concentration in all three solvents. The "water white" oil shows no change in apparent molecular weight with change in concentration in any of the three solvents. It is interesting to note that the sulphur dioxide extract behaves similarly to triphenylmethane and shows a marked increase in apparent molecular

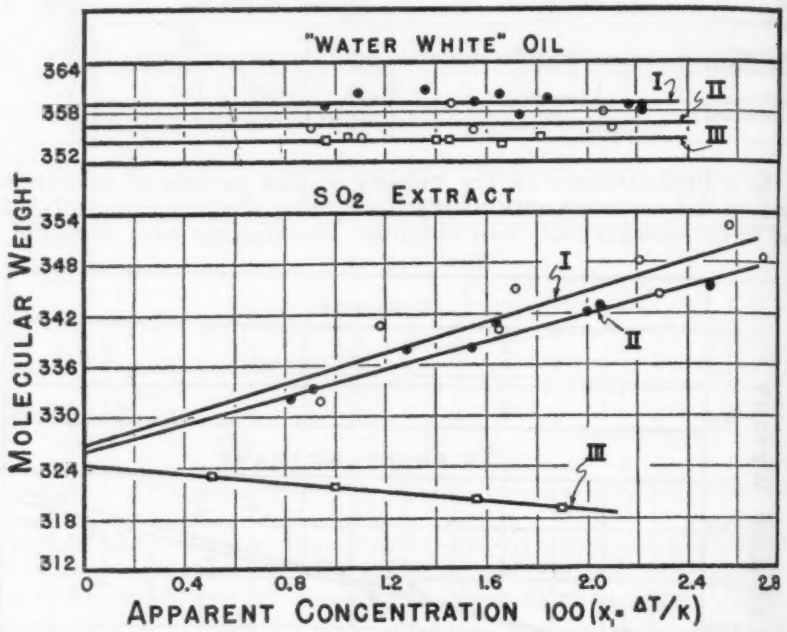

FIGURE 4.—*Molecular weights as a function of apparent concentration in mole percent for a "water white" oil and a sulphur-dioxide extract in "isooctane", n-heptane, and benzene.*

○, ●, and □ represent values in "isooctane", *n*-heptane, and benzene, respectively.

weight with increasing concentration in "isooctane" and heptane, and a slight decrease in benzene.

VI. CONCLUSION

In table 5 is given a summary of the molecular-weight data. These data obtained with pure hydrocarbons representative of the most divergent types in petroleum indicate that extrapolation to infinite dilution gives correct molecular weights within 1 percent. In cases where very high deviations from ideal solution laws occur, it may not always be possible to make precise measurements at sufficiently low concentrations to permit extrapolation to the true molecular weight with the desired accuracy. Such cases seem very unlikely except when nonhydrocarbons are used as solvents.

TABLE 5.—*Summary of molecular weight data*

Solute	Solvent	Maximum deviation of values from extrapolation line	Molecular weight	Theoretical molecular weight	Percent deviation from theoretical (or average)	Remarks
		Percent				
Biphenyl	Benzene	±0.6	153.7	154.08	−0.26	Little if any change in molecular weight with increasing concentration.
Triphenylmethane	Benzene	±.6	242.6	244.14	−.63	Slight decrease in molecular weight with increasing concentration.
	"Isooctane"	±.6	243.6		−.21	Marked increase in molecular weight with increasing concentration.
	n-heptane	±.8	244.1		−.02	
			[1](243.4)		−.29	Do.
				Avg mol. wt	Percent dev. from avg	
Water-white oil	Benzene	±.15	354.6	356.8	−.34	No change in molecular weight with increasing concentration.
	"Isooctane"	±.65	356.6		−.06	Do.
	n-heptane	±.4	359.2		+.67	Do.
Sulphur-dioxide extract.	Benzene	±.1	324.6	325.7	−.34	Slight decrease in molecular weight with increasing concentration.
	"Isooctane"	±1.0	326.7		+.30	Marked increase in molecular weight with increasing concentration.
	n-heptane	±.53	325.9		+.06	Do.

[1] Average in 3 solvents.

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WASHINGTON, November 13, 1934.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP773

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ELECTROLYTIC OXIDATION OF XYLOSE IN THE PRESENCE OF ALKALINE EARTH BROMIDES AND CARBONATES

By Horace S. Isbell and Harriet L. Frush

ABSTRACT

It has been found that calcium, strontium, and magnesium xylonates can be prepared by electrolytic oxidation in a manner analogous to that used for preparing calcium gluconate and can be separated as crystalline salts in good yield from the electrolyzed solutions. Crystalline calcium and magnesium xylonates are new substances which may prove useful intermediates for the preparation of other substances such as threose or trihydroxyglutaric acid.

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I. INTRODUCTION

In a previous publication [1] a process was described for the oxidation of aldose sugars which consisted in passing an electric current through the solution containing the sugar, a bromide, and calcium carbonate.[2] The bromide by electrochemical decomposition yields bromine which reacts with the sugar, regenerating the bromide, so that a small quantity will facilitate the oxidation of a large amount of the sugar. By adding calcium carbonate and the sugar at a suitable rate, and separating the calcium gluconate as it crystallizes from the electrolyte, the process becomes continuous,[3] thereby giving a very simple method for the preparation of calcium gluconate. Inasmuch as xylose is one of the more abundant sugars, several years ago the authors began the study of methods for oxidizing xylose and separating the resulting xylonic acid. Originally the application of the electrolytic process to xylose was limited by the fact that calcium xylonate was not known in the crystalline state and hence

[1] Isbell and Frush. BS J. Research 6, 1145 (1931) RP328.

[2] One of us conceived this process early in 1928 and finally the procedure described in the reference cited in footnote 1 was evolved. In the meantime E. L. Helwig, of Röhm & Haas Co., and R. Pasternack, of Chas. Pfizer & Co., conceived similar processes and filed U. S. patent applications which were placed in interference with the application of Isbell. U. S. Patent No. 1937273 has now been issued to Helwig, and U. S. Patent No. 1976731 has been issued to Isbell.

[3] Isbell, Frush, and Bates. BS J. Research 8, 571 (1932) RP436.

it was necessary to separate the xylonic acid as a basic calcium xylonate. The use of the basic salt is disadvantageous because the strong alkali causes degradation of any unoxidized sugar, thereby reducing the efficiency for continuous operation. After many unsuccessful attempts to obtain crystalline calcium xylonate we applied the electrolytic oxidation method to xylose in the presence of strontium carbonate and prepared a considerable quantity of strontium xylonate.[4] As strontium salts have limited application, the crystalline magnesium salt [5] was prepared and found to be obtained readily by the electrolytic method. A solution containing the barium salt was also prepared, but all attempts at crystallization failed. While this work was in progress attempts were made to bring calcium xylonate to crystallization. Finally this was accomplished by one of us.[6] Since the new salt forms crystals which can be separated readily from the mother liquor, it is now possible to prepare pure crystalline calcium xylonate in any amount by the electrolytic process described in detail for the manufacture of calcium gluconate.

TABLE 1.—*Electrolytic oxidation of xylose* [1]

Electrolyte containing—	Oxidation after—							
	25 hours		40 hours		45 hours		60 hours	
	Oxidation	Anode current efficiency	Oxidation	Anode current efficiency	Oxidation	Anode current efficiency	Oxidation	Anode current efficiency
	%	%	%	%	%	%	%	%
$CaCO_3$ and $CaBr_2$	61	98	95	95				
$MgCO_3$ and $MgBr_2$	59	95	90	90	97	87		
$SrCO_3$ and $SrBr_2$	55	89	78	78	84	75	97	65
$BaCO_3$ and $BaBr_2$	61	98	95	95	[2] 98	92		

[1] 0.75 mole of xylose in 1,500 ml of water saturated with CO_2 and containing the substances given in the first column.
[2] This sample was taken after 43 hours.

The results obtained in typical experiments on the oxidation of xylose in the presence of calcium, magnesium, strontium, and barium carbonate are given in table 1. In general, the current efficiency is high but occasionally lower current efficiencies are obtained, as in the experiment in which strontium carbonate was used. This lower efficiency is not characteristic of strontium, as subsequent oxidations in the presence of strontium carbonate gave higher efficiencies. Occasionally in the preparation of the calcium, barium, and magnesium salts the efficiency is lower than that cited. The cause of these small variations is not known.

II. EXPERIMENTAL DETAILS

1. OXIDATION METHOD

A series of electrolytic oxidations of xylose was conducted under like experimental conditions except that different alkaline earth carbonates and bromides were used. In each experiment 112.5 g

[4] This work was done prior to the publication of Hockett (J. Am. Chem. Soc. **56**, 994 (1934).
[5] Isbell. U. S. Patent No. 1964734 (1934).
[6] Isbell. NBS J. Research, **14**, 305 (1935) RP770.

of xylose (0.75 mole) and 0.06 mole of alkaline earth bromide were added to 0.4 mole of alkaline earth carbonate suspended in 1,500 ml of water and saturated with CO_2. The mixture was placed in a 2-liter 3-necked flask, cooled with running water, and equipped with a mechanical stirrer and two graphite electrodes 2.25 cm in diameter, which were immersed to a depth of 8.6 cm. A 1-ampere current was employed which required about 15 volts. The anode current density was 1.5 amperes/dm^2. The direction of the current was reversed several times during the oxidation in order to dissolve the deposit which formed on the cathode. At various times, as given in table 1, the amount of unoxidized sugar was determined by analysis, from which the amount of oxidation was calculated. In all cases the predominant product was the alkaline earth salt of xylonic acid. The calcium, magnesium, and strontium salts were separated in the crystalline state.

2. PREPARATION OF CALCIUM XYLONATE

The electrolyzed solution obtained as outlined above from the oxidation of 112.5 g of xylose in the presence of calcium bromide and calcium carbonate was filtered and the filtrate evaporated in vacuo to about 150 ml. After seeding with crystalline calcium xylonate considerable crystalline material formed, which was not separated until after adding about 50 ml of methyl alcohol and allowing the solution to stand for several days in order to increase the yield. In this way 110 g of crystals was obtained. The product after recrystallization from hot water was substantially pure calcium xylonate, $Ca(C_5H_9O_6)_2.2H_2O$. The mother liquor after evaporation of the alcohol was light-colored and suitable for repeating the process by the addition of xylose and calcium carbonate. At 20° C, 27.7 g of the salt dissolves in 100 g of water.

3. PREPARATION OF MAGNESIUM XYLONATE

The electrolyzed solution obtained as outlined above from the oxidation of 112.5 g of xylose in the presence of magnesium bromide and carbonate was filtered and the filtrate evaporated in vacuo to a thick sirup, which crystalized to a nearly solid mass after standing a few days. This material was triturated with methyl alcohol, collected on a filter, and dried. The crude product was then recrystallized from 150 ml of boiling water and air-dried at 30° C. The resulting product (122 g) was substantially pure magnesium xylonate, $Mg(C_5H_9O_6)_2.3H_2O$. The yield was approximately 80 percent. Subsequent preparations have been made in which electrolyte, after concentrating to a sirup and seeding with crystalline magnesium xylonate, yielded satisfactory crops of nearly pure product without the use of alcohol. The product was recrystallized from water and air-dried.

Analysis calculated for $Mg(C_5H_9O_6)_2.3H_2O$: MgO, 9.87; H_2O, 13.24. *Found:* MgO, 9.85; H_2O, 13.40. In 6 percent aqueous solution, $[\alpha]_D^{20} = +14.70$. About 30 g of magnesium xylonate dissolves in 100 g of water at 20° C.

4. PREPARATION OF STRONTIUM XYLONATE

The electrolyte obtained by the oxidation of 112.5 g of xylose in the presence of strontium bromide and carbonate was filtered and the filtrate evaporated in vacuo to about 150 ml. Methyl alcohol was added to the solution until it was slightly turbid, and it was seeded with crystalline strontium xylonate. Crystallization began at once. After standing overnight the crystals were collected on a filter, washed with ice water, and air-dried (114 g). The product was nearly pure strontium xylonate. After one recrystallization from hot water, in 5 percent solution, $[\alpha]_D^{20} = +9.8°$.

Analysis calculated for $Sr(C_5H_9O_6)_2.5H_2O$: H_2O, 17.74; Sr, 17.26. *Found:* H_2O, 17.71; Sr, 17.32. This product appears to be the same as that reported by Kiliani;[7] it appears to differ in the amount of water of crystallization from the product reported by Allen and Tollens.[8]

WASHINGTON, January 22, 1935.

[7] Kiliani. Ber. Deut. Chem. Ges. **59**, 2462 (1926).
[8] Liebigs Ann. Chem. **260**, 306 (1890).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP774

Part of Journal of Research of the National Bureau of Standards, Volume 14, March 1935

A PRECISION CATHETOMETER

By Charles Moon

ABSTRACT

A cathetometer which was built for the special purpose of measuring the length of single-layer inductance coils is described. The instrument is suitable for precise measurements of length by comparison with a standard scale. Two microscopes with micrometer eyepieces are carried on a vertical shaft which is supported by a self-aligning type of ball bearing at the bottom and a V-block type of bearing at the top. These bearings allow the shaft to turn easily on its axis with no tendency to bend the shaft and thus vary the distance between the microscopes. A brief discussion is given of the error caused by inaccurate focussing which was especially troublesome in measuring the length of inductances.

A cathetometer suitable for precise measurements has been built for the special purpose of measuring the length of inductance coils which are in the form of single-layer solenoids. It is a wall-type instrument intended only for measuring an unknown length by comparison with a calibrated line standard. A brief description is given because it may be useful to those who may have similar measurements to make.

The instrument is shown in figure 1 as used in measuring the length of a helix of wire. The two micrometer microscopes are carried on a steel shaft 1.5 inch in diameter. The shaft is supported by a lower bearing which rests on the table and an upper bearing which is screwed to the cabinet holding the inductance coil. The weight of the vertical column and the two microscopes is carried by the lower bearing which is a double-row ball bearing of the self-aligning type. The outer race of this bearing is set in a brass collar which has a loose radial fit in the base plate, so that a small horizontal adjustment can be made in any direction by means of four screws. The upper bearing consists of a hardened ball at the end of the shaft which is held lightly in a hardened V-block by a thin bronze spring.

The vertical column rotates very easily and smoothly and may be accurately stopped at two positions by holding the arm A against either the tangent screw S_1 or S_2 by means of the thin spring B at the end of the arm. S_1 is set for readings on the helix and S_2 for readings on the line standard.

The excellence of the instrument is attributed to the bearings and the stopping device which allow an easy shift in position with no tendency to flex or stress the column in any way, and thus change the relative position of the two microscopes.

Each microscope is mounted on a sliding carriage C with means for leveling. The carriage C is connected to a second carriage D by a screw which gives a small vertical adjustment. Both C and D can be securely clamped to the vertical column.

The microscopes are fitted with vertical illuminators and light sources which move with the telescopes. A 6-volt frosted bulb

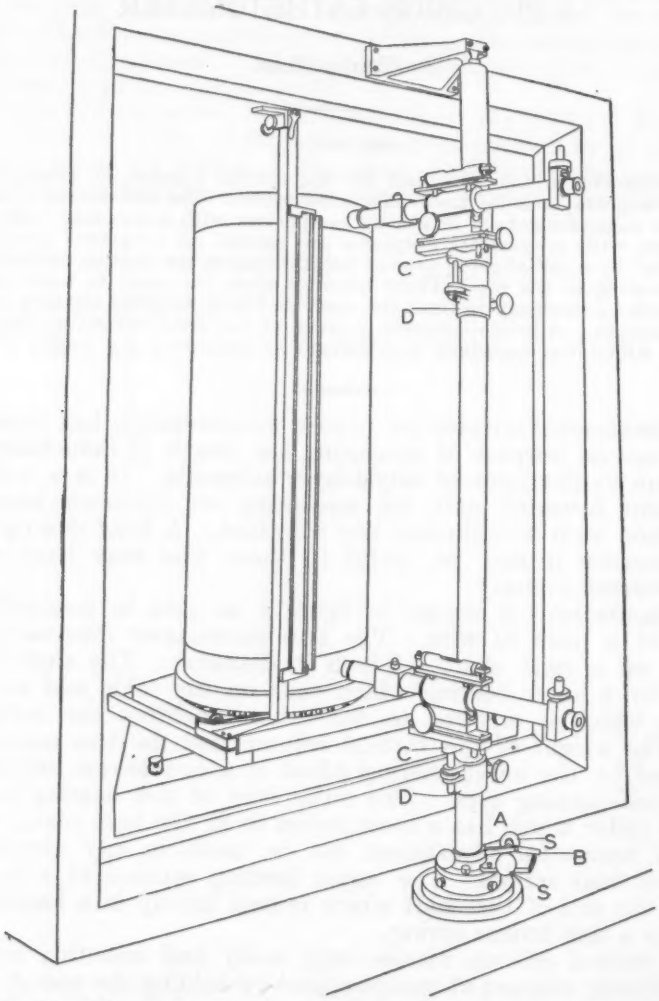

FIGURE 1.—*Precision cathetometer as mounted to measure the length of a single-layer solenoid.*

with a condensing lens and a green gelatine filter is placed in a short tube fixed at right angles to the microscope tube. The light falls on a thin glass plate tilted at an angle of 45° so that it is reflected out through the objective to the ruled surface or wire. This type of illuminator, which allows the entire objective to be used, is greatly superior for these measurements to the type using a 45° prism which covers approximately one-half of the objective.

The adjustments of the cathetometer and sources of error are similar to those of any cathetometer of the comparator type. The source of error which is most difficult to eliminate in measuring the length of an inductance coil is that caused by faulty focussing of the microscopes.

With an aplanatic objective all rays from a given point will be brought to focus at a second point conjugate with the first. If the plane of the crosshairs is exactly at the focus a correct reading of the position of the object will be obtained whether the whole or a part of the objective is used. If the plane of the crosshairs is within the focus, the image formed by a pencil of rays through the upper margin of the objective will be displaced upward, and the image formed by a pencil through the lower margin will be displaced downward. If the plane of the crosshair is beyond the focus, the displacement in each case will be in the opposite sense.[1] In practice, the displacements may be increased by chromatic abberation,[2] spherical aberration, and coma,[3] in the lens used. With an apparently good focus, the displacements of as much as four microns have been observed using a 4-inch objective.

While the difficulties from focussing are well known to a few, there is little discussion in the literature and unfortunately there seems to be no accepted method of determining when the focus is correct.

In this work, the most useful method of focussing was that of Cornu and Benoit [4] in which the focus is adjusted by trial until the same reading of the micrometer is obtained when the light is caused to pass through opposite margins of the objective by means of a movable diaphragm. The improvement when using this method is mostly in the focus on the wires. On the line standard, where the accuracy of focussing can be judged roughly by the constancy of the calibration of the filar micrometer, the results of a series of calibrations after focussing by the Cornu method are not much more uniform than the results of another series obtained when the focussing was done by simply adjusting for best definition.

Another useful method of focussing is to adjust the microscope until no parallax results when the light source is moved.[5] Optically, it is similar to the method of Cornu.

The instrument, equipped with microscopes having objectives of 10-centimeter working distance, has been used in making measurements on two different solenoids. When the column has been turned and brought back to its original position, the difference in the reading of each microscope has always been less than the error of observation. This indicates that the distance between the microscopes and the elevation of the instrument as a whole are maintained with a high order of precision.

WASHINGTON, September 24, 1934.

[1] Cornu and Benoit. Travaux et Mémoires du Bureau International des Poids et Mesures **10**, 12 (1894). See also J. Guild. Proc. Phys. Soc. (London), **28**, 242 (1915–16); Natl. Phys. Lab. Collected Researches Repts., **13**, 229 (1916).
[2] J. Guild. *Chromatic parallax*. Natl. Phys. Lab. Collected Researches Repts., **14**, 249 (1920); also Proc. Phys. Soc. (London), **29**, 311 (1916–17).
[3] Benoit and Guillaume. Travaux et Mémoires du Bureau International des Poids et Mesures, **10**, 35 (1902).
[4] See footnote 1.
[5] Wolff, Shoemaker, and Briggs. Bul. BS **12**, 432 (1915) S256.